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REPORTS
OF THE
PROGRESS OF APPLIED CHEMISTRY.

GENERAL; PLANT; MACHINERY

By W. B. Davidson, Ph.D., D.Sc., F.I.C.,

Consulting Chemist, Newcastle-on-Tyne.

As regards large schemes requiring new plant and machinery in the chemical industry during the past twelve months, one is, from all accounts, justified in stating that the year 1920 has been a lean one.

The importance of having the best type of plant for chemical processes can hardly be overestimated. The cost of repairs and maintenance is largely dependent on the design of the apparatus, and a balance must be struck between this and the saving in labour and efficiency before a proper decision can be arrived at as to the most economical installation. Naturally, the more elaborate and complicated designs are the more costly to instal and also to maintain, but in many cases simplicity and cheapness are synonymous with failure. It is a great mistake on the other hand to choose an appliance just because it is novel and mechanically attractive.

When it is remembered that in some processes the capital charges and costs of depreciation make up about 40 or 50% of the net cost of the product, the value of perfected plant and high efficiency will be fully appreciated.

Improvement in design is achieved almost entirely by taking lessons in the hard school of experience. How many cases can we call to mind of absolute failure of processes of mushroom growth for which the plant had not been carefully thought out, and where the promoters were in blissful ignorance *of the pitfalls and difficulties* that were soon to land them in *a hopeless mess? This is* just where our former enemies, the Germans, have the great advantage over us as regards many chemical processes.

We must not, however, lose sight of the fact that our country would be in a poor way but for the pioneering work, and pioneers do not always succeed as well as their enthusiasm warrants.

Boiler Plant.

In sixty works engaged in different branches of chemical work the average steam raising efficiency has been found to be only 53% as against a possible 70–80%.

The faults mentioned are :—Boiler grates are usually too long ; too little fuel is burned per square foot of grate area ; insufficient advantage is taken of economisers even when these are provided; and far too little attention is paid to the measurement of the feed water, the weighing and analysis of the fuel and the determination or recording of carbon dioxide in the waste gases.

How many chemical works keep proper records of the efficiency of their boiler plants ? Very few, we fear. It is high time this state of things changed for the better.

In the electrical industry we find a pleasingly different state of things. Here there is a continual striving after better thermal efficiency. The latest development in this country is the recent installation by the Newcastle Electric Supply Company of high pressure water-tube boilers at North Tees. These boilers have a working pressure of 450 lb. per sq. in. and supply steam to turbines of large size. The economisers, instead of heating the boiler feed water, heat the air for the furnaces. A notable reduction in fuel consumption is anticipated.

A promising process of low temperature carbonisation has been brought out (Merz and McLellan, Michie, and Weeks' patents) with the object of extracting the valuable tar oils and motor spirit from coal by a quick method of distillation by means of a rapid current of superheated steam. In this process the coal that would otherwise go direct to the mechanical stoker of the boilers is continuously fed into the top of a vertical retort of large section, through the bottom of which steam, bled from the low pressure side of the turbines and then strongly superheated, passes carrying with it the tar oils and gases to a heat exchanger where the latent heat of the steam is transferred to the boiler feed water. The hot coke is directly and continuously fed to the stoker.

We hear that high efficiency is being obtained in the United States on trial plants with turbines actuated by mercury vapour in combination with steam. On the other hand, processes are mooted for the recovery of waste heat by the utilisation of low-boiling fluids, such as pentane and ammonia. In the latter case advantage is sought in working low-temperature boilers with the waste gases which, in the case of the best-designed boiler plants, are not reduced in temperature by heat exchange below about

360° F. before reaching the chimney stack. With gas and Diesel engines the temperatures of the exit gases are much higher and give still greater scope for economy.

In gas works it has been usual to find a great quantity of heat passing away unused in the waste heat flues which as they leave the retort settings are generally red hot. Now that a low calorific value standard may be declared under the new Gas Regulation Act of August, 1920, gas undertakings, especially those provided with vertical retorts, have, in several cases, begun to turn this source of heat to good account by the use of waste heat boilers for the raising of low pressure steam to make a large proportion of water-gas from the red hot coke in the retorts, and thus materially increase the total yield of gas.

Even then, as in the most economical power station, a large amount of low-temperature heat goes up the chimney to waste. For the economical extraction of the bulk of this low-temperature waste heat we are still waiting for a suitable design of plant.

Little is heard of the Bonecourt gas-fired surface combustion boilers which, from their high efficiency (92% has been claimed), ought now to find favour where gas at a low price is available. One would have thought there would be a large field for such boilers in coke-oven works where a large proportion of the gas—usually 50%—is available after heating the ovens by its means. This is generally utilised in firing ordinary Lancashire boilers or in running gas engines.

H. Warschafski[1] describes a highly efficient electrically heated vertical boiler containing a number of vertical small-bore tubes of insulating material. Resistances between top and bottom electrodes form the means of heating; alternating or three-phase current up to pressures of 10,000 volts may be used. An output of 80,000 kg. of steam per 24 hours has been obtained with a consumption of 1000 kilowatts, representing an efficiency of about 95%. In this country the cost of electricity would require to come down to less than 0·1d. per unit before such a process could be looked at.

A common source of waste in boiler plants is the faulty arrangement of steam jet forced blast. D. Brownlie[2] gives the results of the investigation of 250 boiler plants. Of these 37% were fitted with steam jet blowers. The steam used by the jets varied from 1% to 20% of the total produced, the average being 6·6%. It is pointed out that properly arranged blowers should not consume more than 3–4%, while in many cases it would be better to replace the jets by mechanically-induced draught which takes on an average 2½% of the steam produced.

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[1] *Chem.-Zeit.*, 1919, **43**, *Rep.*, 242 ; *J.*, 1919, 935A.

[2] *Engineering*, 1920, **109**, 71 ; *J.*, 1920, 143A.

It is almost impossible to burn coke by itself in a boiler without forced blast or extra good draught. A mixture of coal and coke is much easier to burn. The "Nicol Sandwich System"[3] of feeding in a layer of coal on the top of the coke appears to have been very successful and to have acquired popularity during the past year even in electric power stations.

W. H. Owen[4] has patented a method of heating the air for combustion by the waste gases. After an initial heating part goes direct under the fire-bars, and part after further heating is supplied above the fire-bars.

Furnaces.

The commonest type of furnace, the ordinary open domestic fire-place, has received scientific attention from Dr. Margaret Fishenden.[5] According to tests made, the radiant efficiency of coal burnt in different types of grates varied from 19½ to 24%—much higher than most of us have been led to expect. Anthracite gave an efficiency of 27, coke 28½, low temperature coke about 33, briquettes 19, as compared with coal in a certain trial at 24%.

Economy is advocated by building flues on inner walls, by restricting the draught, and avoiding recessing the grate too much. Taking the total heating efficiency of a coal fire at 30%, that of a modern gas fire at 60%, and that of an electric heater at 100%, and the respective costs at 45s. per ton of coal, 4s. 6d. per 1000 cb. ft. of gas, and 1d. per unit of electricity, it is calculated that the ratios of the costs of coal, gas, and electricity for domestic heating are as 1 : 3 : 5.

In industry each kind of fuel has its own field. Electricity is incomparably the best agent in the manufacture of special and high-class steel. According to D. F. Campbell[6] the quantity of energy used on electric furnaces in Britain in 1914, excluding those used for aluminium, was less than 6000 h.p., but on the day of the Armistice the total was more than 150,000 h.p., of which 18,000 h.p. was working on the reduction of chromium and tungsten ores, and the remainder on steel. In the re-melting of steel turnings and nickel-chrome steel, in the manufacture of rustless steel and low-hysteresis iron for transformers, electric furnaces have very special advantages. Unless electricity is supplied at a low price, however, it cannot compete with coal for ordinary work. Not many months ago at a steel works in Yorkshire the writer was informed that most of the electric furnaces were being discarded on account of the high consumption of current and the prohibitive cost of this.

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[3] *Gas J.*, 1920, **152**, 209.

[4] E.P. 150,065; *J.*, 1920, 382A.

[5] "The Coal Fire." *See J.*, 1920, 334R.

[6] *J.*, 1920, 224T.

Similarly, in spite of the many advantages of gaseous firing, the fuel cost will always be a chief factor in determining whether it will succeed in ousting coal or coke. Immense strides were made in gaseous firing in industrial centres during the war. In Birmingham, for example, according to C. M. Walter,[7] the consumption of gas for industrial heating for the year 1912–13 was 609,000,000 cb. ft. (the gas made from 50,000 tons of coal), whereas for the year 1918–19 it amounted to 2,520,000,000 cb. ft. (the gas made from 200,000 tons of coal).

Much progress has been made in the design of gas-fired furnaces, especially in regard to using recuperation and thereby effecting economy of fuel as well as achieving a higher temperature. The simplest method of recuperation employed is to preheat the secondary air by passing it through flues arranged in the bed of the furnace. In other cases the secondary air is heated by the waste gases in specially built regenerators on the counter-current principle, but this action is comparatively slow in taking effect.

Very effective furnaces are those of the reversing regenerative type arranged with two sets of recuperators, so that while one set is carrying away the waste gases and absorbing the heat therefrom, the other set is giving up its heat to the incoming secondary air.

When the temperature required does not exceed 1000° C. good average town gas at ordinary pressure may be used, without air blast or recuperation. For higher temperatures air blast or recuperation is necessary; high-pressure gas at 10 or 12 lb. per sq. in. may also be used if a public supply is available, but it is not profitable for the private consumer to go to the expense of compressing.

The principal uses to which gas is put in industrial work are :—Melting of solder, lead, typemetal, brass, bronze, aluminium, aluminium alloys; for tinmen's stoves, japanning, and lacquering stoves; glass-melting tanks, gloryholes, ceramic firing kilns; annealing, case-hardening, carburising, calorising, and all other kinds of heat treatment of steel, etc.

Here it may be noted that the impending general reduction in the heating value of town gas may necessitate the alteration in the design of some kinds of gas-fired furnaces. When the reduction is due to the addition of inert gases, nitrogen and carbon dioxide, there will be an inevitable drop in flame temperature, which may be compensated by the use of air blast or recuperation.

A new type of experimental recuperative gas-fired furnace is described by W. Rosenhain and E. A. Coad-Pryor.[8] This works with natural draught and gives temperatures up to 1650° C. The air used for combustion passes through carborundum tubes into a collecting chamber and then into a mixing or combustion chamber where it meets coal gas. Magnesite and zirconia bricks are stated to be inferior for use in this furnace to good firebricks washed over with a mixture of carborundum and fireclay.

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[7] *Gas J.*, 1920, **152**, 208.

[8] *Trans. Ceram. Soc.*, 1918-19, **18**, 467; *J.*, 1920, 213A.

An ingenious, though somewhat complicated, reversible, gas-heated furnace has been patented by F. T. Rennison.[9] The reader is referred to the diagram.

What appears to be a useful furnace setting for heating large metal pots or stills has been designed by F. H. Nickle.[10] There are three annular spaces for the furnace gases. The intermediate one is the combustion chamber which passes its gases on to the inner chamber and thence up and around the vessel to be heated to the outer annular space.

Centrifugal Machines.

Reference is made to certain types of machines under the head of "Filtration."

The machine patented by E. D. Mackintosh[11] appears to be an ingenious one. The bottom of the centrifugal basket consists of an inner part, sliding on the inner sleeve, and the outer frustum of a cone, the outer edge of which is normally in contact with the lower rim of the side wall to close the basket. The bottom is pressed upward by a pair of toggle levers, controlled by a spring which tends to open them and force the basket upwards, the centrifugal force also tending to open the toggles. On stopping the basket the solid matter by its weight forces the bottom down and is thus discharged.

The grading centrifugal separator patented by R. A. Sturgeon[12] also appears worthy of close study.

Drying Apparatus.

There is the usual large number of patents for drying different classes of materials. We may cite as being of probable interest the design of A. Gerlach.[13] This is a revolving drum dryer which is provided with longitudinal bars of cruciform section placed in such relative positions that the material to be dried falls freely four times during each revolution.

In another form of cylindrical dryer, patented by W. Greding,[14] there are a number of grooves constructed on the periphery in planes normal to the axis. The material to be dried is conveyed to the grooves and the cyinder is surrounded by an endless perforated band resting against the projections between the grooves and moving with the same velocity as the drum.

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[9] E.P. 137,977 ; *J.*, 1920, 214A.
[10] U.S.P. 1,329,470 ; *J.*, 1920, 215A.
[11] U.S.P. 1,321,766-7 ; *J.*, 1920, 215A.
[12] E.P. 134,158 ; *J.*, 1920, 935A.
[13] E.P. 133,327 ; *J.*, 1920, 143A.
[14] G.P. 313,148 ; *J.*, 1920, 257A.

On the subject of filters there are also a great many patents for the year 1920, brought out mostly in the United States, where remarkable advances in the science of filtration have been made in recent years. Reference may be made to the continuous vacuum filters of A. E. Alexander[15] which admit of withdrawing filtrate and wash liquors separately, and wherein means are provided for inflating the filter bags at an appropriate stage, thus bringing them in contact with scrapers for the removal of the filter cakes.

There are several important papers on the general subject of filtration.

H. B. Faber[16] gives a concise account of American methods of filtration, describing the Moore leaf-type, the Moore multiple-compartment rotary filter, the ordinary rotary filter, and the rotary hopper de-waterer.

G. Schmitt's[17] paper describes a process of filtering at very high pressures up to 300 atmospheres, capable of dealing with very fine sludges.

At the fourth conference of the Chemical Engineering Group of the Society the subject received special attention. In a paper on "The principles of technical filtration" E. Hatschek[18] gives a great deal of valuable practical information in concise form. The interesting use of filter-plates made of carbonised materials, such as ground coke and pitch, for dealing with acids is referred to amongst other things. In "The filtration of colloids," by W. R. Ormandy,[19] it is stated that, generally speaking, particles of matter exceeding 0·0001 mm. in diameter will eventually settle from the solution, and this size happens to be about the limit of microscopic visibility. Particles below this limiting size do not settle out because the molecular and electrical forces outweigh the action of gravitation. Filtration by a process of electro-osmosis is dealt with. R. A. Sturgeon[20] claims for his self-discharging centrifuges a large capacity, low power consumption, and a high filtration standard of clarification. Figures are given in the original paper to show how efficiency of clarification increases with the speed of rotation. It is pointed out that there is a vast field for continuous self-discharging centrifuges for dealing with fine solids. S. H.

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[15] E.P. 136,309 and 141,001; *J.*, 1920, 391A.

[16] *J.*, 1920, 21T.

[17] *Chem.-Zeit.*, 1920, **44**, 657, 669; *J.*, 1920, 681A.

[18] *J.*, 1920, 226T.

[19] *J.*, 1920, 228T.

[20] *J.*, 1920, 230T.

Menzies[21] describes the "Sharples Super-centrifuge" and points out that with this machine separation of solid matter is by subsidence and not by filtration. A small diameter and large depth and high speed are its distinctive characteristics. It would not appear to be so suitable for dealing with liquors heavily charged with solids as for finishing purposes. The clarification of glue and of nitrocellulose liquors, the separation of wax from mineral oil and of vegetable oils from soap stock, and the dehydration of water-gas tar are among the operations the machine is said to perform successfully. B. Bramwell[22] deals with the design of mechanical filters intended principally for the filtration of water for drinking purposes, with special reference to the "turn-over" filter. In a paper on "Recessed plate and plate and frame filter-presses," E. A. Alliott[23] contributes a long and exhaustive treatise on the usual standard British type of filter-press.

Under the general title "The properties of powders" the question of the caking of salts is fully dealt with by T. M. Lowry and F. C. Hemmings.[24] It is pointed out that caking is largely caused by moisture, water occluded in crystals, polymorphism, and the presence of hygroscopic impurities. It occurs most readily in soluble crystalline salts, in deliquescent substances, in crystalline hydrates, and in substances that are liable to decompose in the presence of moisture. In some cases, like that of ammonium sulphate, it is essential to remove all trace of acidity, so as to ensure a dry non-caking salt. Trouble is minimised by reducing the soluble impurities, by agitation during drying, by drying after the operation of grinding which is known to release moisture, by carrying out the drying at moderate temperatures, by packing the cooled material in a dry atmosphere, and by maintaining as constant a temperature as possible during storage.

The conditions favouring the formation of coherent pellets is a subject requiring further study.

Electrostatic Precipitation.

There is a large crop of patents on devices for electrostatic deposition of dust.

A novel method of removing the dust from the settling surfaces is that patented by H. Püning,[25] whereby a whistle, syren, or similar appliance sets up sound waves of sufficient intensity to cause dislodgment.

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[21] *J.*, 1920, 231T.

[22] *J.*, 1920, 232T.

[23] *J.*, 1920, 261T.

[24] *J.*, 1920, 101T.

[25] G.P. 315,534 ; *J.*, 1920, 322A.

In a patent by Siemens-Schuckertwerke G.m.b.H.,[26] a method is described of removing dust from blast furnace gas or the like by passing the gas through a number of electrodes consisting of frames in which are mounted several series of pivoted plates, arranged either horizontally like a venetian blind or vertically. In alternate frames the plates are inclined in opposite directions to give repeated changes of direction to the gas, and serve as precipitation electrodes and high potential electrodes respectively.

The large electrostatic separation plant at Skinningrove started operations in April, 1920. It was erected for the Skinningrove Iron Co. by Messrs. Simon-Carves, Manchester, on the principles of the Lodge methods of precipitation and to the designs of the Lodge Fume Co., Birmingham. The gas is dealt with at the rate of about 100,000,000 cb. ft. per day, measured at 200° C., being the blast-furnace gas made from about 500–600 tons of coke. This is in the hot state, and the aim is to precipitate the great bulk of the dust without appreciable loss of heat. It was not intended to clean the gas sufficiently well to allow of its use in gas engines without further treatment. The final cleaning is effected in water-spray washers.

The total amount of dust precipitated and dealt with is about 50 tons per week. About 27% of this is potassium chloride, the other soluble salts being about 8% each of sodium and calcium chlorides. The dust is extracted by hot water and the solution filtered systematically by four rotary vacuum filters. The insoluble dust is returned to the furnaces while the potassium chloride is separated from the other salts by a carefully controlled continuous system of evaporation and fractional crystallisation where the best advantage is taken of the varying relative solubilities of potassium and sodium chlorides over the temperature range 25°–100° C.

The gas entering the precipitators contains 5–6 grams of dust per cb.m. and the gas leaving, 0·8–1·1 grams (with only 80 to 85% of the plant at work). This efficiency of cleaning—about 82%—is all that was anticipated and is regarded as sufficient to effect large savings in many ways, such as :—

1. Increased thermal efficiency of stove, boiler and other furnaces by elimination of the usual heavy deposits of dust in flues, checkers, and regenerators.
2. Increased duty from plant.
3. Reduced labour costs for cleaning.
4. Preservation of firebrick from corrosion by alkalis contained in the dust of the blast-furnace gas.
5. Saving in fuel.
6. Recovery of a valuable by-product in the form of potassium chloride.

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[26] G.P. 315,931; *J.*, 1920, 476A.

The voltage used is about 50,000 but this is variable and depends on the dust load in the gas to be treated. The velocity of the gas in the foul main is very high—100 feet per second; in the precipitating chambers it is 2 to 3 feet per second, the drop in pressure through the chambers being about ½ inch water gauge.

The temperature of the gas entering the chambers is 220°–250° that of the gas leaving, 200°–220° C. The total consumption of power is at the rate of only 50 kilowatts.

The building is 128 feet long, 31 feet wide, and 65 feet high and consists of three entirely distinct ferro-concrete structures The chambers are 16 in number, each being 31 ft. × 7 ft. 6 in. × 23 ft. high from hopper mouth to roof. They are worked in paralle and each is provided with inlet valve, double outlet valve for regulating the flow, and a mushroom valve. There are four explosion doors at either end, a manhole with explosion door in the roof, and a dust discharge valve in each of the two dust bins with which each chamber is provided. In each unit there are two discharge grids arranged in series, and each grid is provided with its own electric transformer set. Each grid is provided with tapping gear, operated by levers, which are worked every eigh hours during the cleaning operations when the gas and electric currents are shut off. The dust drops into the hoppers and thence passes to scraper plate conveyors delivering to the extraction plant. The ferro-concrete structure has been found satisfactory in working at the temperature of 250° C.

This is the first large plant for electrostatic precipitation to b erected in this country, and its success is gratifying. It is, of course possible to recover practically all the dust and attain an efficiency of, say, 99·9%, but the additional cost of plant to effect this would probably not be justified in a case of this kind.

The Cottrell type of precipitator is to be found doing good servic —chiefly in the separation of acid mist and the dust contained therein—in chemical works in the United States and Germany and was also used on some of the acid concentration plants erected in this country by the Ministry of Munitions.

In their paper on "The theory of gas scrubbing towers wit internal packing," F. G. Donnan and I. Masson[27] seek to obtain simple mathematical expressions for the experimental study o the factors governing the design of such towers. In course of th discussion it was stated that solid spheres as packing took up 74% of the total capacity of the towers, while 1-inch rings in sheet meta took up only 8%. The paper shows in a quantitative manne how good absorption efficiency depends on: High interfacia area between gas and liquid; high relative motion between ga and liquid (within limits); high degree of turbulent motion o gas or liquid or both; sufficient rate of flooding to produce maximum drip effect.

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[27] *J.*, 1920, 236T.

A curious but probably effective method of promoting the atomising of liquids, or solids dissolved or suspended in them, has been brought out by H. Seiferheld.[28] This consists in dissolving a gas in the liquid and so raising its vapour tension considerably. Solids may first be dissolved and the solution treated in the same way. In the application of the method to the atomising of water in sulphuric acid chambers or for washing gases in the contact process, sulphur dioxide is dissolved in the water before atomising. The process admits of application to liquids other than water.

A novel method for the rapid cooling and crystallising of hot solutions is that patented by Maschinenbau A.-G. Balcke.[29] A series of endless bands circulates through the hot solution. While the lower part of each band is immersed the upper part is subjected to a current of cold air and the crystals that form are removed before re-immersion.

On the subject of gas cleaning, a patent is published by L. B. Fiechter.[30] This describes an apparatus consisting of a rotating flat screen over which the granular filtering material is distributed. From this it is removed continuously or intermittently, and may be elevated, purified, and returned to the screen.

Rings for filling absorption towers, distillation columns, or the like are described in a patent by R. Lessing.[31] Each ring is provided with a diametrical partition extending the whole or part of the way across. Excellent fractionating results have been obtained with this type of packing, which gives a maximum of contact surface and free gas space.

An improvement in apparatus for the raising of liquids by direct fluid pressure has been patented by J. E. L. Ogden.[32] This ingenious type of automatic pump is deserving of special attention. It can be used with great advantage for such purposes as the recovery of condensed water from steam traps etc.

What may be a useful method of separating oil from water in emulsions is published by C. W. McKibben.[33] The emulsion is made to follow a tortuous path between two vertical concentric pipes placed in a tank. The space between the pipes is occupied by a series of discs with openings near their axis and peripheries alternately. It may be of advantage to heat the inner pipe.

To separate from a liquid a substance which is soluble in it at normal temperatures but insoluble at low temperatures, P. T.

[28] G.P. 302,554 ; *J.*, 1920, 740A.

[29] G.P. 319,968 ; *J.*, 1920, 563A.

[30] G.P. 317,254 ; *J.*, 1920, 477A.

[31] E.P. 139,880 ; *J.*, 1920, 322A.

[32] E.P. 136,900 ; *J.*, 1920, 92A.

[33] U.S.P. 1,327,835 ; *J.*, 1920, 180A.

Sharples[34] adopts a method of cooling the mixture to a temperature at which the substance separates, and centrifuging it with a liquid which is heavier than the substance and not miscible with it. The substance floats on the heavier liquid and is separately discharged. This process can be applied to the separation of wax from mineral oil by means of brine.

An important paper on "The action of concentrated sulphuric acid on iron" has been contributed by C. E. Fawsitt.[35] It would appear to be safe practice to use steel or cast iron for sulphuric acid of a strength of over 82%, that is, where lead cannot be used. The action of 89% acid on steel as stated in the paper is remarkably slight, and, as the author remarks, it would be interesting to examine the effect of concentration on the velocity of the corrosive action for strengths between 88 and 91%. Contact of the steel with such metals as mercury, platinum, and aluminium, contrary to expectation, did not cause a marked increase in the rate of reaction.

A method of coating autoclaves and other vessels of metal or wood with bakelite to prevent corrosion by acids is patented by Arnstädter Malzfabrik.[36]

On the subject of lubrication there is an interesting contribution by H. M. Wells and J. E. Southcombe on "The theory and practice of lubrication: the 'Germ' process."[37] The authors seek to find a satisfactory explanation of "oiliness" but their explanation does not satisfy their critics.

They demonstrate that: (1) Capillary effects (hitherto ignored in lubrication) play a fundamental part. (2) The presence of fatty acids in an oil lowers the surface tension of the oil against water. (3) A neutral glyceride possesses a similar tension to a neutral mineral oil. (4) The addition of a relatively minute amount of a fatty acid to a neutral mineral oil reduces the tension to that of a commercial animal or vegetable oil or compounded lubricating oil.

The authors appear to come to the conclusion that interfacial tension is the basis of "oiliness." They have found by experiment that the coefficient of friction is reduced by the addition to mineral oils of small amounts of selected fatty acids, and they have shown that fatty compounded oils are unnecessary for many purposes of lubrication, that fatty oils are not essential, and that fatty acids can entirely displace fatty oils for compounding. On the results of their tests they base what they call the "germ process" of compounding one or more fatty or other acids with one or more mineral oils. They claim that many of the old formulæ and specifications for compound oils are obsolete, and that for gas engines, steam cylinders, crank cases, turbines, and marine engines the "germ process" oils have been completely successful.

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[34] U.S.P. 1,351,265; *J.*, 1920, 682A.

[35] *J.*, 1920, 147T.

[36] G.P. 304,319, 305,176, 307,699; *J.*, 1920, 53A.

[37] *J.*, 1920, 51T.

Bearing on this same subject is a paper on "Wetting power and its relation to industry," by W. H. Nuttall.[38] The author shows that for a liquid to possess a high wetting power it must have a low surface tension and also a low interfacial tension, but that surface tension alone is not a reliable indicator of the wetting power. An emulsion of an oil in any liquid always possesses good wetting properties, he points out, and one method of measuring wetting power is by comparing the emulsifying power of the liquid with regard to a standard oil. In many industries wetting power plays an important part. One of the most interesting instances is the flotation process for the separation of minerals. This is making great strides and now enables low grade tailings to be profitably extracted and is also used in washing out the dirt from small coal. The process is based on the fact that the same liquid wets a mineral sulphide or coal differently from quartz or pyrites, and this difference in "wettability" is accentuated by the addition of a small amount (1 lb. per ton) of a suitable oil, or in some cases acid or alkali. The good material is elevated on the foam which is formed by aeration, leaving the gangue behind.

Still another carbon dioxide automatic indicator has been placed on the market and is said to be reliable in its action. This is the W. R. CO_2 indicator. It is certainly robust in design and simple in its action, which depends on the diffusion of the gases through a porous pot, and the absorption of the CO_2 by an internal cartridge of soda-lime. The draught necessary to work the apparatus is very small, the excess of chimney over the boiler flue draught being sufficient.

A most interesting and highly ingenious instrument has lately been brought out by the Cambridge Scientific Instrument Company. It is called the katharometer, and is the product of the brain of Professor Shakspear of Birmingham University. It tests the purity of gases in the most rapid manner and requires only a few c.c. for the purpose. It was first successfully used for determining the purity of hydrogen, but can probably be used with advantage for other gases where the mixtures are not complex. It consists essentially of two short thin platinum spirals heated to about 90° C. One of the wires is immersed in a standard gas, say, dry air, and the other in the sample of gas to be tested. The difference in temperature of the wires causes a difference in electrical resistance, which is measured and forms the basis for the determination of the percentage of impurity. The difference in temperature is brought about by molecular bombardment of the platinum wires, and is a function of the density of the gas in question.

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[38] *J.*, 1920, 67T.

FUEL.

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The question of the utilisation of fuel has been dominated in 1920 by the continued and almost world-wide shortage. In this country supplies have fallen far short of demand, prices have risen, and above all stood the disturbing threat of a strike culminating in a fourteen days' stoppage in autumn. There are small grounds for hope that the days of cheap and abundant fuel are to return. The coal consumers' most effective remedy would, therefore, seem to be to meet dearness and scarcity by economy in consumption. The pressure of these economic conditions is reflected in the great activity in fuel technology to-day, and manifold efforts are being made to achieve a more rational use of coal.

In considering the possible methods of dealing with coal—and by that one must have in mind more particularly in this country bituminous coal—an ideal process must satisfy three requirements :—(1) The heating power of the coal to be applied with the maximum thermal efficiency. (2) The operation to cause a minimum pollution of the atmosphere. (3) The chemical values of the fuel to be utilised as well as possible, having regard to all the circumstances. Never has so much attention been focussed on all these points as now—both in the laboratory and in industrial practice.

Fuel Research.

While previously it was left to isolated individual workers, in this country the institution of a department specially to teach and investigate fuel technology was first made at Leeds University in 1907. Later the Imperial College of Science in London embarked upon a similar enterprise ; now the work is being pursued in various centres—Manchester, South Wales—and the Government has instituted the Fuel Research Board equipped with an extensive experimental station at Greenwich. This year the University of Sheffield has also established a professorship in Fuel Technology and Chemistry of Coal Mining, which is held by Dr. R. V. Wheeler.

A similar pursuit of fuel research abroad is evident, and attention should be directed to the Coal Research Institute at Mülheim, Westphalia—one of the so-called Kaiser Wilhelm Institutes—erected just prior to the outbreak of the war, and placed under the direction of Professor Franz Fischer. It appears to have been founded primarily to make chemical and physical investigations of coal and other fuels. The main object has been described as the conversion of relatively inert raw coal into soluble and more reactive substances, the development of extraction processes and the extension of the study of the carbonisation process to varying conditions of pressure and temperature. The Institute being opened within a few days of the outbreak of hostilities in 1914, the investigations there conducted bear evidence of influence of war-time exigencies in the prominence given to the production of liquid fuels and lubricants from coal. Four volumes, containing the records of more than one hundred researches of varying importance, have been published under the title, "Gesammelte Abhandlungen zur Kenntnis der Kohle."[1] These are typical of what may be regarded as German scientific mass production. Broadly speaking, they cover a variety of problems of coal chemistry, although sometimes in a superficial manner. Interesting fundamentals seem to have been perforce dropped in favour of war-time necessities. There is, however, a great accumulation of chemical observations on coal and lignites which makes the volumes well worth reference by workers in the same field. No detailed survey will be made of their contents—this is better done in the Journal's abstracts—but it may be stated that to the recognised reagents for extracting and treating coal they have added at least two—ozone and liquid sulphur dioxide.[2] By means of the former coal can be brought almost completely into solution, while it was found to disintegrate at once in the latter. The possibilities opened out by this sort of reagent seem considerable. The conversion of naphthalene into liquid fuels is another achievement.[3] Of the great number of coal-tar constituents few only are commercially separated in the pure state. The higher tar oils have a more restricted application; they are difficult to fractionate and this is reflected in the relatively lower commercial value. The chemical exploitation of naphthalene—hitherto of relatively small value and mainly as a fuel only—may presage the opening out of a new chemistry of the heavy tar oils. The volumes contain a considerable amount of information on the extraction of coal and lignites. The pressure of war-time needs for oils is evidenced by the prominence given to low-temperature distillation experiments in the third volume. A form of laboratory apparatus was devised[4] consisting essentially of an externally heated revolving cylindrical retort in which the coal could be distilled with or without steam, as necessary. With this apparatus a survey has been made of coals from different regions then accessible, when distilled at low temperature. Those from the Saar coalfield[5] gave the highest yields of liquid products—as much as 15% by weight of the coal being obtained. The fragility of the coke obtained was unpromising except when this is to be used for dust firing. It is known that the tars from gas-producers of the Mond type fitted with a bell are of the low-temperature character and Saar coals are said to give good yields in such producers when suitably modified. Altogether these researches form the most extensive study of low-temperature distillation published, and considerable efforts have already been made to exploit them industrially. Several patents for low-temperature distillation processes in revolving retorts have been published as a consequence and even disputes as to priority have arisen. One should not, however, pass without noting that J. A. Yeadon and W. Adgie, of Leeds, distilled coal in a revolving retort many years ago, although their work seems to have been premature.[6]

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[1] *Cf. J.*, 1919, 399A, 400A, 492-495A, 523-529A, 532A, 564A, 565A, 672A, 855A, 938A; 941A, 1920, 54A, 55A, 93A, 96A, 146A, 150A, 151A, 218-224A. 258-260A, 288A, 291A, 324A.

[2] *Cf. J.*, 1916, 1001.

[3] *Ann. Repts.*, 1916, 1, 13.

The Fuel Research Board set up by the British Government has issued its Third Report for the years 1918 and 1919,[7] in which the completion of the experimental station at East Greenwich is announced. The plant is on a considerable scale with laboratories attached and it is hoped to make exact studies of various fuel processes and a survey of British coals. In particular the possibility of producing larger quantities of liquid fuels and smokeless solid fuel by suitable methods of carbonisation is to be probed. The Fuel Research Board has other activities which will be referred to later. A group of industrial interests has combined under the name Midland Coal Products, Ltd., to establish an experimental station in Nottinghamshire[8] for the study of low-temperature carbonisation processes, continuing the work initiated by the Petroleum Investigation Committee of the Ministry of Munitions in 1916. There is no doubt that the focussing of so much attention by independent observers on this much-discussed problem is to be welcomed. Much harm has resulted in the past from premature attempts at financial exploitation of processes which have not been technically perfected. The economics of carbonisation are complex and the material and financial balance sheets require to be treated

[4] *Ber.*, 1919, **52**, 1035; *J.*, 1919, 563A.
[5] *J.*, 1920, 259A.
[6] E.P. 19,183, 1889; *J.*, 1890, 797; E.P. 22,292, 1891; *J.*, 1893, 31
[7] *J.*, 1920, 151R.
[8] *Gas J.*, 1920, 151, 289.

as a whole and not from the point of view of one product only—whether solid, liquid, or gaseous—as has so often been the case. Conditions are changing with time. Actual and prospective demands for liquid fuels give a new importance to schemes for preserving the volatile matter of coal in liquid forms, and therefore to unbiassed studies of the merits of individual processes. Reference may be made to the "Carbocoal" process[9] which is to be introduced in this country and for which much is claimed.

The Fuel Economy Committee of the British Association[10] and that of the Federation of British Industries[11] (the latter Committee having been initiated this year to study and improve the efficiency of industrial heating operations) may both be mentioned as showing the interest now awakened in these matters in many quarters.

There is no doubt that this many-sided movement to effect a more rational utilisation of fuel by scientific study is a characteristic of the post-war epoch and mainly a consequence of the war itself. It will be contrary to experience if some of these efforts are not fruitful in the coming years, leading to an increased thermal economy of fuel processes and possibly to a smoke-free atmosphere even in industrial districts.

GAS REGULATION ACT, 1920.

In Great Britain the passing of the Gas Regulation Act of 1920[12] will probably prove the outstanding feature of the year in the field of rational fuel utilisation. The British town's gas industry has grown to great proportions in its century of existence, first of all as an agency for the distribution of light, but becoming in the last generation predominantly a purveyor of heat, owing to the change of circumstances, technical, economic, and social. Nevertheless, in the eyes of the law it remained primarily a lighting industry until the outbreak of war. For almost the whole of the gas consumed its intrinsic illuminating power had become of secondary importance. Nevertheless, the statutory restrictions were such, in effect, as to require that the gas must be made in a certain way so as to yield a self-luminous flame. This legal stricture collapsed owing to the exigencies of war-time conditions and the munitions industries, and as a result of the experience gained it became clear that both economic and technical considerations prohibited the re-establishment of the former and now archaic statutory regulations. The Government was able to take advantage of the Fuel Research Board to obtain independent advice as to what was technically sound, and at the same time just to the various interests concerned. The opinions of the Fuel Research Board expressed in its Third Report (1920) have now been substantially incorporated in the Gas Regulation Act of 1920.

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[9] *Ann. Repts.*, 1918, **3**, 38 ; *J.*, 1921, 4R.

[10] *J.*, 1920, 308R. *Cf. infra.*

[11] *Gas J.*, 1920, **151**, 232.

[12] *Gas J.*, 1920, **151**, 292; *J.*, 1920, 240R.

It is too soon to see the full consequences of this change, but it places the commercial transaction between the producer and consumer of gaseous fuel at least on a logical and comprehensible footing, for the latter will in future be charged according to the heating value received. For the purpose of charging, the commercial unit of heat will be 100,000 B.Th.U., to be known as one therm. The Act also contemplates the possibility of making the charges depend on the readings of recording gas calorimeters. Though the continued reliability of gas calorimeters has hitherto been insufficiently established, Sir George Beilby has had under observation for some time the instrument devised by Simmance. Whether a reliability has been found for this or any other instrument such that legal penalties might rightly depend on its accuracy or inaccuracy is not clear from the Fuel Research Board's report or any information published, and an open mind should be kept in the meantime. This is a matter of great financial importance and doubtless will receive the necessary study before binding decisions are taken. There is scope for much skill in the construction of a satisfactory recording gas calorimeter. Certain difficulties with water-flow instruments have been avoided in the Thomas calorimeter,[13] in which air is substituted as the calorimetric medium. It is then possible to maintain a constant ratio between the volumes of gas burnt and air heated, pressure and temperature effects being eliminated. According to the Act gas must be supplied purified and at a minimum pressure, usually 2 inches of water. It is proposed to make an enquiry into the question of the desirability of setting statutory limits to the percentage of carbon monoxide and incombustible constituents. Both are points on which action should be preceded by careful enquiry. With regard to the incombustible constituents, experience may show that no legal limitation is necessary, for while incombustible constituents are undesirable, a certain proportion is in practice inevitable, and the mere sale of gas on a heat basis removes any incentive to increase the proportion present. It provides, indeed, an inducement to reduce all thermally useless constituents because they have to bear the cost of distribution without producing revenue in return. With these restrictions a gas undertaking will have the right to choose and declare the calorific value it intends to work to, and also to change it later after giving due notice, provided always that it alters or replaces the consumers' appliances so that they are capable of burning the gas safely and efficiently. The experimental evidence available justifies this step. The three reports of the Gas Investigation Committee of the Institution of Gas Engineers on the question[14] have shown that within wide limits, the thermal efficiency of different grades of gas in use is not markedly affected by the calorific value, provided that the rate of supply of heat units is maintained, and the Act is based upon this principle of thermal equivalence. It is, however, important to the consumer that the declared heating power be closely adhered to, whatever it may be. The Act also provides for the supply of power gas, the inking up of gas undertakings, and the purchase and sale of supplies n bulk from one area to another so as to promote the more efficient utilisation of available supplies—*e.g.*, from coke ovens—and also the better organisation of manufacture. Although the consequences of this new legislation are not yet to be estimated, one tendency is already evident, *i.e.*, the closer examination of gas-making processes from the point of view of thermal efficiency, which cannot but result in the promotion of national fuel economy. The law has made it possible for the most efficient processes to be adopted when and as discovered even if not now practicable or known.

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[13] *Gas J.*, 1920, **152**, 387.

No one familiar with the technology of fuel would dogmatise as to the methods of twenty years hence, and it is right that the Government, while regulating the gas industry as is necessary for a public service, should still have left room for desirable technical progress.

NATIONAL FUEL ECONOMY.

The publication of the Coal Conservation Committee's Report in 1918,[15] and especially the section on power generation, led to the dissemination, at least among uncritical and non-technical readers, of the idea that in the interests of coal conservation, the national supply of heat, light, and power should be made by the medium of the electric current. The fallacy of this, so far as British conditions go, induced many criticisms of which the most extensive and complete was probably a Report to the Institution of Gas Engineers prepared by Sir Dugald Clerk, A. Smithells, and J. W. Cobb.[16] This Report formed the subject of discussion at the Institution of Electrical Engineers, London.[17] Several signatories of the Power Sub-Committee Report spoke at this meeting. It appeared that responsible electrical engineers did not seriously question the validity of the statements of comparative thermal efficiencies in the Report, but insisted rather on other factors which operate in the selection of one or other agent for power, lighting, or heating. C. H. Merz stated that the signatories to the Power Sub-Committee's Report were dealing with the production of power from coal and did not regard it as extending to the distribution of heat. Furthermore it was not his experience, that where the development of electrical operation had proceeded to the greatest extent, as in Chicago, the use of gaseous fuel had been curtailed. He disclaimed for the Committee the idea, popularly seized upon, that the generation of electrical power should be confined to sixteen stations. Rather was the country to be mapped out into sixteen areas for standardisation of conditions of supply and distribution. While it is satisfactory to find that the views of this Power Sub-Committee are more restrained and justifiable than generally imagined, it is regrettable that their report of such national importance should have been so loosely worded in the first place, as to lead to the misconceptions[18] erroneously held by the general public and in some official circles, that these misconceptions should have remained uncorrected for three years, and that the Coal Conservation Committee should apparently have passed lightly over the problem of the efficient distribution and utilisation of heat, for which purpose so much of the national expenditure of coal is incurred.

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[14] *Cf. Trans. Inst. Gas Eng.*, 1918, 1919, 1920; *J.*, 1920, 508A.

[15] *Ann. Repts.*, 1917, **2**, 48; 1918, **3**, 38; 1919, **4**, 39.

[16] *J.*, 1919, 104R; *Ann. Repts.*, 1919, **4**, 39.

[17] *Gas J.*, 1920, **150**, 778.

POWER PRODUCTION AND STEAM RAISING.

When the Coal Conservation Committee reported in 1918, it hesitated to commit itself as to the desirability of combining by-product recovery with electrical power generation, but left the matter open for further investigation. Since then the Nitrogen Products Committee of the Ministry of Munitions has issued its Report[19]—a *magnum opus*—on the fixation of nitrogen. To a great extent this deals with the costs of production of power, on a large scale under modern conditions and under many conceivable systems. Most significant is the conclusion that the wide and popular belief in a great pecuniary gain and economy of fuel to be made by combining recovery of by-products with power generation on a large scale is illusory. They find no promise of certain advantage in either respect over a steam-driven plant using raw coal.

In respect of coal consumption they find[20] that if any existing form of by-product treatment precede the combustion of fuel under steam boilers, the coal consumption will be increased by an amount varying from 32 to 150%, and with regard to capital costs the position is worse, while the cost of the kilowatt-year will probably also increase except in special cases which would be financially very sensitive to the value of by-products. The scale of working postulated was 100,000 kw. and for this the coal treatment plant would be of a magnitude exceeding any now existing, involving unsolved engineering and, one may add, financial problems. It is scarcely practical politics to-day. One interesting alternative, the combination of gasworks with gas distribution system and generating station using the coke, is not worked out, although this seems to be more likely of immediate practicability and perhaps financial soundness. The erection of several large new gasworks, in contemplation to meet the growing demand for the gaseous and liquid products of carbonisation, may make an increased supply of carbonised fuel available for power generation. Gaseous fuel commands to-day an average price of 10d. per therm, whereas if burnt under steam boilers its value is only one tenth as much. If by-product recovery is to precede power generation, the method chosen should be one which makes the best use of all products. The possibilities are tentatively referred to in the Report[21] which mentions the generation of power at the L.C.C. tramways station from gas coke, under the so-called "Sandwich system." A. L. C. Fell[22] reports extended experience that when mixtures of 50% of coal with 50% of coke are burnt, the plant worked efficiently and with a monetary saving as against coal. W. T. Kerr[23] claims to have run the Hereford electric power station on coke and breeze achieving the lowest fuel costs of any station in the country. There is, however, a limit to the supply of such cheap fuel as coke breeze and the use of coke seems to be attracting wider interest among power station engineers.

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[18] D. Clerk, *Gas J.*, 1920, **151**, 133.

[19] *Cmd.* 482 ; J., 1920, 25R.

[20] *Loc. cit.*, 23.

K. Wilkens[24] proposes to effect a carbonisation of coal by the sensible heat of the products of combustion from a steam boiler furnace on their way to the economiser. This attempt to combine carbonisation with steam boilers may be compared with the suggestion of Merz and McLellan, A. C. Michie, and E. G. Weeks[25] to carbonise coal prior to combustion for power generation by superheated steam taken from a turbine.

D. Brownlie has published further collections of data on numerous steam boiler plants, work which is now particularly opportune when fuel economy is a matter of national as well as individual concern. In his Bulletin No. 2[26] he gives the results of observations on the steam consumption of the steam-jet blowers fitted to ninety-three installations. These consumptions ranged from 1% to 20% of the steam generated with an average of 6·7%—about double of what is necessary. He has given[27] the results obtained in trials of eighty mechanically-fired Lancashire boiler plants. He found a mean efficiency of 59% and concluded that they were on an average not more efficient thermally than hand-fired plants. The advantages were in other directions, *e.g.*, improved conditions of labour. In another communication[28] he reports the results of tests on sixty boiler plants attached to chemical works, finding an average efficiency of 58%—rather less than the general average of plants typical of all industries. He concludes from the examination of hundreds of boiler plants that the economy of fuel to be achieved by simply running existing steam plants in accordance with the rules of good practice might reach millions of tons per annum.

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[21] *Loc. cit.*, 116.

[22] *Electrician*, 1920, **85**, 396.

[23] *Electrician*, 1920, **85**, 472.

[24] *Mitt. Verein Elektrizitätswerke*, 1919, **18**, 241 ; *J.*, 1920, 394A.

[25] E.P. 117,290, 118,777, 136,868 ; *J.*, 1918, 490A, 646A : 1920. 150A.

[26] *Engineering*, 1920, **109**, 71 ; *J.*, 1920, 143A.

[27] *Proc. Inst. Mech. Eng.*, 1920, 263.

C. E. Stromeyer[29] emphasises the necessity for studying steam requirements for power and heating together wherever possible. If the steam used to generate power in a steam engine leaves at considerable pressure, this exhaust steam may then be utilised for heating purposes and the fuel consumption per h.p.-hour becomes very small, say ⅓ lb. of coal. He discusses the application of this method to a number of cases. An alternative method of combining heating and power supply is furnished by the use of gas engines, which deliver their exhaust to a suitable waste heat boiler. The Bonecourt boiler with the tubes fitted with spiral packing has found an application in this direction. As compared with the use of steam engines this method of combining heat and power supply has the advantage of eliminating the handling of solid fuel in the factory.

PEAT AND LIGNITE.

The stringency in coal supplies has led to a closer scrutiny of alternative fuels. P. F. Purcell, whom the Fuel Research Board has appointed Peat Investigation Officer, has reported on the peat supplies of Ireland.[30] The present consumption of peat in Ireland is 6-8 million tons per annum, and of coal 4,740,000 tons. At this rate of consumption the peat deposits would not be exhausted in less than five hundred years. The average calorific value of the air-dried peat is 6850 B. Th. U. per lb., ash content 3%, nitrogen 1–2·5%, and the yield of sulphate of ammonia in by-product working should reach 100 lb. per ton. Air-drying still remains the only method which is certainly feasible, and, of course, the removal of water (90% when cut) by a commercially practicable method is the first great problem. The moisture in air-dried peat is usefully employed when the peat is gasified in producers. It is hoped by studying the exploitation of a bog where conditions are most favourable to obtain authoritative data. The addition to the area of cultivable land by the clearance of bogs is a factor which may be of greater importance in future.

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[28] *Chem. Tr. J.*, 1920, **67**, 247, 311, 343 ; *J.*, 1920, 681A.

[29] *Manchester Steam Users' Memorandum for* 1918-19 ; *J.*, 1920, 97R.

[30] *Special Report No. 2, Fuel Research Board* ; *J.*, 1920, 213R.

Increased interest has been awakened in lignite, which occurs very widely. Although this fuel is of little importance under British conditions, some attention has been given to the deposits in Devonshire as a source of power. The most extensive exploitation both as fuel and as a source of by-products is found in Germany, where the production steadily increases. The fuel after removal of excessive moisture and briquetting has excellences rarely found in coal supplies at this day; it is uniform in chemical composition and physical condition, low in ash, and is therefore extensively employed for many purposes, even in districts adjoining the coalfields. It is proposed to set up a well-endowed research station in Berlin[31] to study further possible developments in the use of brown coals both for fuel and by-products.

The location of coalfields on the east and west of Canada has led the Dominion government to study the utilisation of lignite deposits in the central provinces, but the problem there does not seem easy. Lignites vary so much in character that processes successful at one place cannot be transferred simply to another.

W. A. Bone[32] proposes to dehydrate lignites by passing hot flue gases over them at a temperature just short of incipient carbonisation.

WATER POWER.

The subject of water power, whether from tidal energy or water falls, may be regarded as germane to the fuel problem; the new interest in it is symptomatic of the post-war conditions. The Water Power Resources Committee of the Board of Trade[33] recommends that water supplies should be placed under public control and believes that considerable undeveloped resources exist in Great Britain.

More recently the Ministry of Transport has published a suggested scheme for regulating the Severn estuary by a dam, carrying a road and railway, and then to utilise the energy of the tidal fall for generating electricity. This may be compared with a proposal to harness the tides in France.[34] Apart from technical engineering problems, such proposals raise the question as to whether the cost of fuel has risen sufficiently to justify the great capital outlay involved.

DOMESTIC FUEL.

Domestic fuel, which amounts to 35-40 million tons of coal annually, is one of the principal items in the British fuel bill, and therefore deserves more attention than it has received in the past, especially as it is responsible for more than its due share of the smoke nuisance. At the outset of this report it was laid down that an ideal fuel-using process should be such as to cause a minimum atmospheric pollution, and this aspect of the fuel problem at last seems to be receiving the attention it deserves. A Smoke Abatement Committee set up by the Government in 1914 has been revived by the Ministry of Health and has issued a Report[35] dealing with domestic smoke. The harm caused by smoke is dealt with under various headings, hygienic, æsthetic, and financial. Perhaps the realisation of the enormous monetary damage of smoke will stimulate public interest which has proved indifferent to the other considerations. The Committee concludes that for cooking, for heating water, or for warming rooms, gas and coke form practicable alternatives to coal, and that for the open fire grate the difficulties in the way of preparing a carbonised fuel are likely to be overcome. Even to-day we could, if we chose to take advantage of available processes and appliances, make an enormous reduction in domestic smoke. A more far-sighted policy on the part of our municipalities than hitherto would be helpful. Too often the gasworks and power station have been regarded primarily as keystones in the fabric of the city budget and not as weapons to combat smoke and waste. Cheapening of smokeless fuel and electrical power would be most effective.

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[31] *J.*, 1920, 238R.

[32] E.P. 130,455; *J.*, 1919, 709A.

[33] *Second Report*, 1920, *Cmd.* 776; *J.*, 1920, 260R.

[34] *J.*, 1920, 357R.

An intensified scientific study of domestic appliances is another welcome phase of activity in fuel research, for without well-ascertained data on which to base it, effective national action is unlikely to be taken. The publication by the Fuel Research Board[36] of Mrs. M. W. Fishenden's research on "The Coal Fire" is opportune. Initiated under the auspices of the Manchester Corporation Air Pollution Board, the work has at last supplied some basis of fact as to the capabilities of the open grate. Most important is the measurement of the "radiant efficiency" of the fires determined by the method devised for the study of gas fires at the University of Leeds.

The astonishing result was found that the proportion of the heat of the fuel radiated varied little from fire to fire, whether of old or modern construction, being for coal 20–24%. The superiority of the newer grates seems due largely to the restriction of the flue outlet which curtails the flow of air through the room, thus making comfortable conditions more easily attainable with the consumption of less fuel. The construction of the newer fires with restricted air supply below and little ironwork to cool the fuel mass by conduction, enables smaller fires to burn satisfactorily and more slowly. The results with different fuels are interesting. In a fire which had a radiant efficiency of 24% with coal, anthracite gave 27%, dry gas coke 28·5%, but this advantage was lost if more than 10% of moisture was present. Two dry cokes made by carbonisation at low temperatures gave 31 and 34% respectively. Briquettes of coal were relatively inefficient with only 19%. This emphasises one difficulty which obstructs the commercial development of low-temperature carbonisation, viz. the friability of the coke which renders transportation difficult. If this has to be overcome by briquetting, the superiority as a fuel for open grates will apparently be more than wiped out. By measurements of the volume and temperature of the products in the chimney the importance of regulating flue draught to secure efficient use of a fire was shown. (Incidentally Mrs. Fishenden showed that no measurable improvement was made by treating a fuel with the powders—usually coloured common salt—which are so largely advertised.) It should be remembered that the fire is credited in these tests with the whole of the heat radiated from lighting to dying out. It is only, therefore, when burning for long periods that the users of a fire can even approximately take advantage of such proportion of radiated heat as stated. It has been suggested that by adding the heat passing up the flues and conducted thence to the general fabric of the building, the fire might be credited with an efficiency of 60–70%. The heat passing up the chimney is not wholly lost. It effects ventilation but is relatively unavailable for warming and should scarcely be classed with the heat actually radiated into the room, which probably forms the best basis of comparison. The modern gas fire has a radiant efficiency of about double that of the coal fire, but the superiority in this respect is even more pronounced because the maximum effect can be obtained almost at once and fuel consumption cut off instantly.

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[35] *Interim Report*, 1920; *J.*, 1920, 284R.

[36] *Special Report No.* 2; *J.*, 1920, 334R.

This work does give a substantial foundation to the treatment of domestic fuel economy as regards room warming simply, but there still remains the very difficult problem of the more numerous and voracious kitchen ranges serving several purposes in smaller houses, where everything has been sacrificed to obtain the minimum outlay of capital. Under the auspices of the Fuel Research Board[37] A. H. Barker has been making efficiency trials of coal-fired domestic cooking ranges which indicate in general a very low degree of thermal efficiency. It is not easy to contrive an apparatus which shall be capable of efficient adaptation to several incompatible uses. It is also an extremely difficult matter to apply precise tests to domestic cooking appliances, as the same author indicates when outlining his methods of measurement.[38] Nevertheless, some effort is desirable to obtain reliable data on which to base important decisions in such matters as housing.

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[37] *Fourth Report*, 1918-19; *J.*, 1920, 151R.

[38] *Bull. British Commercial Gas Assoc.*, Nov., 1920.

A recent development which, though commercial, may have important technical results, is the amalgamation of the leading firms engaged in the manufacture of domestic and industrial gas-heating appliances, under the name of Radiation, Limited. If, as a consequence, designs are standardised, production costs reduced, and research vigorously prosecuted in the department established for the purpose, gas appliances should find a rapidly widening use. A standardised gas fire has been already worked out, such that the essential parts, radiants, brick, burner, injector and interior castings, are interchangeable, while the external design is left to the individuality of the associated manufacturers. An overall efficiency of at least 65% is claimed, while silence in working is increased and flexibility to widely varying conditions, *e.g.*, of calorific value varying between 300 and 600 B. Th. U., per cb. ft., and of pressure from 15/10–8 in. of water, ensured. The gas cooker has also received attention.

Liquid and Motor Fuels.

The problem of meeting the growing demand for liquid fuels increases in importance and cannot be regarded as solved. Various sources of supply alternative to mineral oil are receiving attention. The distillation of English shales is being attempted commercially, but the removal of sulphur is a difficulty. The carbonisation of coal with a view to conserving liquid products has become prominent (see pp. 20 and 47). The Fuel Research Board is making this one of its chief studies. The economising of heavy fuel oils by admixture of powdered coal—the production of the so-called colloidal fuel—was referred to in last year's Report,[39] and has been brought more prominently to the notice of British oil technologists by L. W. Bates and H. O'Neill.[40] The process will shortly be worked in this country.

The need for volatile motor spirits is even more pressing. Benzol, while a satisfactory substitute for petrol, is produced in quantities limited by the scope of the coking and gas industries. The motor interests urge the extension of benzol production from town gas, but sometimes with the attending destructive proposal of an insufficient price. From the point of view of public gas supply, the removal of benzol from the gas is only justified if thereby the price of the heat unit in gas can be reduced to the consumer, and with the coming of charging on a heat basis one gallon of benzol will commonly be worth 15d. to 18d. as vapour in the gas. In pre-war days the unit of heat in petrol was worth 2–3 times that in town gas, the higher price being due to the special convenience attaching to a concentrated fuel of high volatility. The new Gas

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[39] *Ann. Repts.*, 1919, 4, 29.

[40] Inst. Pet. Tech., Nov. 16, 1920; *J.*, 1920, 395R, 413R.

Regulation Act will ensure that no legal obstacle prevents the removal of benzol from gas if a gas undertaking thinks it desirable and profitable.

Other hopes are centred upon alcohol, the potential supplies of which have been closely scrutinised. E. Bury[41] has evolved a process[42] for the extraction of ethylene from coke-oven gas by strong sulphuric acid followed by conversion into alcohol, but this cannot yet be regarded as established. E. de Loisy[43] has described a variation of the process in which catalysts such as vanadium and tungstic acid are used to facilitate absorption of the olefines. In considering the application of such a process to town's gas, the thermal and financial considerations governing benzol extraction (*cf. supra*) are again operative.

The production of alcohol by fermentation seems to offer the most promising potential source.[44] Sir F. Nathan, who has been appointed Power Alcohol Investigation Officer, has drawn up a memorandum on the prospects. Owing to the conditions governing our food supply there is no prospect of any great extension of alcohol production from vegetable products in this country. Foodstuffs must have a prior claim on agriculture. Molasses is a possible source, but will preferably be used as such in the country of origin. Tropical vegetation offers more possibilities, but even there the cultivation of foodstuffs promises to be more remunerative than raising crops for alcohol. When a supply of cheap raw material is found it will still be necessary to work out a process for its treatment. An Australian scheme with such an object has been described.[45]

A. P. H. Desborough,[46] in a survey of the position, is hopeful that something may be done in this country by the cultivation of such plants as the artichoke on reclaimed land. Then, owing to the rotation of crops, some increase of food production would also be achieved.

At the instance of the Power Alcohol Committee, H. B. Dixon has been examining the physical properties of alcohol, alone and in admixture, which determine its suitability as motor fuel. Some of his results have been already published.[47] Alcohol has the valuable property of forming with other liquids, mixtures having vapour tensions higher than those of either constituent. With benzene the maximum occurs at about 80% alcohol and 20%

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[41] *Gas J.*, 1919, **148**, 718; *J.*, 1920, 94A.

[42] See *Ann. Repts.*, 1919, **4**, 31.

[43] *Comptes rend.*, 1920, **170**, 50; *J.*, 1920, 147A.

[44] *Fuel Research Board Report*, 1918-19, and *Memorandum on Fuel for Motor Transport.*

[45] See *J.*, 1920, 236R.

[46] Brit. Assoc., 1920; *J.*, 1920, 302R.

[47] *J.*, 1920, 355R.

benzene. This increased volatility compensates in some measure for a lower calorific value and is helpful in starting. The high ignition temperature of alcohol under pressure is useful as also the low velocity of propagation of flame through mixtures with air. Alcohol has most of the properties desired in a motor fuel. H. Moore[48] has determined the vapour tensions of mixtures of alcohol with petrol and benzene, and his results agree with Dixon's statements.

Coal gas is now a proved motor fuel, but in the absence of convenient containers, its use has receded to negligible proportions. The tendency to manufacture gas of lower calorific value also operates against its application to motor propulsion, but as Sir George Beilby points out, if carbonisation at low temperatures becomes established on a great scale yielding gas of high calorific value, the situation will be reversed, the fuel capacity of a given container being roughly doubled. Indeed he appears to regard the rational treatment of our coal as the most promising source of motor fuels.

F. Haber[49] suggests the use of acetylene, preferably mixed with another fuel to depress its inflammability.

Coal and coke as fuels for steam-driven heavy vehicles are familiar, but it has been proposed to gasify the fuel and use it in an internal combustion engine. D. J. Smith[50] describes the construction of suitable portable gas-producers. The principal advantage claimed is the extremely low fuel cost—with coal at 40s. per ton, this being equivalent to petrol at 2½d. per gallon. The producer is worked with a thin bed—about 6 in. only—so that volatile matter is completely decomposed and elaborate scrubbing rendered unnecessary. The addition of fuel and discharge of ash go on continuously whereby clinker formation is said to be avoided. The following comparisons are given for a five-ton waggon :—

	Steam.	Petrol.	Producer-gas.
Cost of fuel	50s. per ton.	3s. per gall.	55s. per ton.
Cost per gross ton mile ..	0·31d. ,,	0·66d. ,,	0·048d. ,,
Cost per net ton mile ..	0·75d. ,,	1·20d. ,,	0·091d. ,,

The author admits that the arrangement lacks the convenience of petrol-driven vehicles, but the liquid fuel problem is such to-day that no avenue can be left unexplored. Developments of this unconventional solution will be watched with interest.

GASEOUS FUELS.

Town's gas found its place as an industrial fuel in its application to small-scale work where the advantages were most easily apparent

[48] *J.*, 1920, 78T.

[49] *Z. Elektrochem.*, 1920, **26**, 325; *J.*, 1920, 621A.

[50] E.P. 135,319, 135,643; *J.*, 1920, 146A. Inst. Automobile Eng., Jan. 8, 1920. *Engineering*, 1920, **109**, 59, 92.

of a handy supply of high-grade fuel which could be used to produce high temperatures in simple furnaces without labour and without the complication of regeneration etc. The use of town's gas in the engineering trades has gone a considerable way of late years in the replacement of solid fuel furnaces of quite a considerable size. The saving of labour costs in handling coal and ashes, convenience, and flexibility compensate for the extra price of fuel. In one locomotive building works the heating of large plates for flanging is satisfactorily performed with town's gas and in addition to the advantages mentioned, the output of the press and its attendants is doubled. In this case a subsidiary injection of oil is used to increase the speed of working and ensure a smoky flame. As the size of furnaces using town's gas has grown, increasing the thermal efficiency by the use of regeneration and recuperation has become more important and is occupying the attention of those concerned in design. Some heat is recuperated in melting furnaces by preheating the metal and in larger reheating furnaces the reversing regenerator has been applied with considerable success. In a furnace of this type constructed by Radiation, Ltd., 373 cwt. of marine-engine parts were "once-heated" for forging by the use of 60,570 cb. ft. of gas.[52] The research department of the same firm has been engaged in the study and design of simplified and cheapened furnaces for annealing up to 900° C. with a reduced fuel consumption. Attention has been given to the important question of atmosphere in annealing furnaces. Even if free oxygen is absent, components of the water-gas equilibrium may cause oxidation of iron present, and a determination of the relative partial pressure of these suggested that the conditions may be such as to promote scaling—even when an excess of coal gas is supplied to the furnace. Hydrocarbons were absent from the furnace atmosphere. The conditions during the heating up period seem most favourable to scaling. The use of luminous flame to secure the deposition of a protective layer of carbon on the load at the outset is suggested, and carburetting the gas may be an advantage to increase the hydrocarbons present. White and Hood[51] showed that in a coal-gas-fired furnace—in flame type—decarburisation may proceed even more rapidly than oxidation.

There is no outstanding novelty to record in the field of gas producer practice where recent efforts seem to be directed to the improvement of mechanical accessories. Thus the Power Gas Corporation[52] is developing suspended double-arm pokers, automatic coal feeds and ash removal gear which are claimed to deal satisfactorily with very caking coals, *e.g.*, Durham coals. Such a producer fitted with water chute is reported as giving a throughput of 22 cwt.

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[51] *Gas J.*, 1915, **132**, 138, 312.

[52] Private communication.

per hour, yielding a gas of 40–45% total combustibles, while one with water jacket tested alongside under similar conditions as to fuel and blast pressure gasified 15 cwt. of coal per hour with a considerably lower quantity of total combustibles in the gas.

In this connexion attention may be drawn to the claims made by J. S. Atkinson[53] for the Chapman agitator in use in America. This agitator consists of a water-cooled toothed arm which is caused to revolve just below the surface of the fuel bed 5–10 times per hour, thereby breaking up the caking coal. The main feature is the absence of rigid connexion to the driving gear so that the stirrer "floats" up and down with the alteration of the fuel level or climbs over any unusually hard clinker.

A complete account of the construction and working of a by-product producer gas plant of the Lymn type for power and heating in an engineering works has been given by W. H. Patchell.[54] The plant was designed for the economy of fuel, and gas engines with exhaust boilers were used for generating power. The net coal consumption was 1·51 lb. per kw.-hr., equivalent to a thermal efficiency of 19·9%, a result only achieved by the largest and most efficient of steam-power generating stations (see p. 25).

Attention has been drawn by H. J. Hodsman and J. W. Cobb[55] to the fact that both carbonisation of coal and gasification of carbon with mixtures of air and steam are almost thermally neutral, and that the considerable heat costs of present practice are not inevitable. The limiting efficiency of carbonisation can only be attained by substituting internal heating of the coal for the external heating now used, while the maximum efficiency of complete gasification or gas production in producers will be attainable when oxygen can replace air in the producer blast. The use of oxygen in this manner would probably give an efficiency of 91% for carbonisation and of 90% for gasification. The price of oxygen is a difficulty but this ought to fall rapidly in the near future with the more highly developed technique of gas fractionation. This suggestion has excited most immediate interest in countries where coal is scarce and hydro-electric power cheap—indeed if taken in night hours almost cost-free, owing to the absence of any practicable means of storing electricity. Such cheap power might be used to produce oxygen which could then be employed for gas making. The gas-holder would thus become in effect a means of storing electricity.[56]

The advantage of cheap oxygen and consequent fuel economies would not be confined to the production of gas. The application of gaseous fuels to high-temperature processes would be greatly extended. The need for recuperation would be less frequent and plant could be simplified. F. G. Cottrell[57] has indicated applications to metallurgical practice.[58]

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[53] *J. Soc. Glass Tech.*, 1919, **3**, 148; *J.*, 1919, 394R.

[54] *J. Inst. Elect. Eng.*, 1920, **58**, 417.

[55] *Trans. Inst. Gas Eng.*, 1920; *J.*, 1920, 508A.

[56] *Cf.* W. Geyer, G.P. 319,523; *J.*, 1920, 650A.

E. Terres[59] has compared the use of dried lignite burnt as pulverised fuel with the results obtained when it is first gasified and then used with recuperation of heat. The dust firing had a thermal efficiency of 75·7% and the producer-gas firing 53·3%.

BLAST-FURNACE GAS.

The better utilisation of blast-furnace gas has attracted more attention recently. S. H. Fowles[60] describes a plant installed at a North-East coast iron and steel plant with shipyard. The blast-furnace gas treated by a Halberg-Beth cleaner is used partly in gas engines to drive a 7000 kw. generation plant and the rest for heating purposes. The additional advantages are detailed and the author advocates the wider development of such methods in connexion with public power supply. G. W. Hewson and the same author[61] discuss the advantages and economies of combining coke-ovens with iron and steel plant.

The first application of the electrostatic method of cleaning blast-furnace gas in this country has been made at the Skinningrove Iron Works and a preliminary account of the results has been given by A. Hutchinson and E. Bury.[62] The loss of heat has been comparatively small, and an economy of gas at stoves and boilers was found. About 50 tons of dust (27% K_2O) has been recovered weekly. Potash recovery has provided a new and possibly decisive factor in encouraging the installation of cleaning plant.[63]

J. E. Weyman[64] has described a burner of the Bunsen type for burning gas of varying pressure under boilers, *e.g.*, uncleaned blast-furnace gas. It has a device for automatically adjusting air supply to gas pressure and as a result an increase of efficiency amounting to 33% is claimed.

COMBUSTION.

The Home Office Experimental Station has made further contribution to our knowledge of the phenomena associated with the propagation of flame through gaseous mixtures. W. Mason and

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[57] *J.*, 1920, 321R.
[58] See also J. H. Paterson, *J.*, 1920, 374R.
[59] *J. Gasbeleucht.*, 1920, **63**, 673 ; *J.*, 1920, 774A.
[60] *J. Inst. Elect. Eng.*, 1920, **58**, 431.
[61] *J.*, 1920, 211T.
[62] *J. Iron and Steel Inst.*, 1920, **52**, 65 ; *J.*, 1920, 751A.
[63] H. G. Scott, Cleveland Inst. of Engineers, 1920 ; *Gas J.*, 1920, **152**, 509
[64] *Gas J.*, 1920, **152**, 337.

R. V. Wheeler[65] have studied the propagation of flame in mixtures of methane and air in horizontal tubes, re-traversing ground covered many years ago by Mallard and Le Chatelier, with the much less manageable mixture (CS_2+NO). The effects due to such factors and phenomena as length of tube (whether the ends are open or closed), the production of vibratory movements of flame, uniform movement, and uniform acceleration were brought out. The last effect was observed with long tubes open at both ends, of which mine galleries are industrial examples; the results may be serious for the flame is then less liable to extinction following a vibration of the flame into the cooled products in the rear of the zone of combustion.

W. Payman[66] has investigated further the propagation of flame in complex gaseous mixtures, studying the influence of the percentage of oxygen in the "atmosphere" with which inflammable gas is burnt. Some light was thrown on a well-known phenomenon that the maximum speed mixture of a gas with air contains usually an excess of the combustible gas. This has been attributed, although inconclusively, to the high thermal conductivity of the gas. Payman suggests that it is rather a case of the influence of mass action and finds support for this by measuring the speed of propagation of flame through explosive mixtures of methane or hydrogen with different proportions of oxygen and nitrogen. The "displacements" of maximum speed mixtures from theoretical proportions followed—qualitatively at least—the indications of the mass law. When the mixture consists of methane with oxygen the mass law points to a maximum speed of combustion with the theoretical mixture (CH_4+2O_2) which agreed with the result observed. He also showed that the "speeds generalisation" could be more widely applied than shown in previous papers.

The propagation of flame in mixtures of methane and air in vertical tubes and in streams of mixtures has been studied by W. Mason and R. V. Wheeler.[67] The effect of convection was demonstrated in the former case. In mixtures travelling along tubes at 35–65 cm. per second it was shown that the lower limit mixture contained only 5·02% CH_4 compared with 5·4% required when stationary.

R. V. Wheeler[68] has further investigated the ignition of methane-air mixtures under the influence of the impulsive electrical discharge. He confirmed his previous observations[69] that there is no evidence of "stepped ignition" but that with clean electrodes the relative igniting current in the primary of his induction coil varied in a regular continuous manner with the variations of composition of the mixture ignited, within the limits of inflammability. Wheeler finds himself in opposition to the opinions of several observers.[70]

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[65] *Chem. Soc. Trans.*, 1920, **117**, 36; *J.*, 1920, 181A.

[66] *Chem. Soc. Trans.*, 1920, **117**, 48; *J.*, 1920, 181A.

[67] *Chem. Soc. Trans.*, 1920, **117**, 1227; *J.*, 1920, 778A.

[68] *Chem. Soc. Trans.*, 1920, **117**, 903; *J.*, 1920, 592A.

[69] *Ann. Repts.*, 1917, 2, 46; *Chem. Soc. Trans.*, 1917, **111**, 130; *J.*, 1917, 378.

An interesting method suggested by McDavid[71] for the determination of ignition temperatures by bringing of a soap bubble full of gas into contact with a hot wire of known temperature, has been shown by A. G. White and J. W. Price[72] to be wanting in precision.

The silent burner has great commercial importance in the construction of domestic gas appliances. H. Davies[73] has shown that the mixture with air containing 27% of a coal gas could be burnt most rapidly without producing noise when issuing from all tubes tried, although the actual rate depended on the length and diameter of the tube. H. Hartley[74] has suggested that the 27% mixture probably has the minimum viscosity and therefore is capable of passing through tubes at the maximum speed without the establishment of turbulent motion.

The composition of the products of complete combustion of a fuel is governed by the composition of the fuel and the proportion of excess air. The heat capacities of the products of combustion and therefore the theoretical temperatures of combustion depend on the composition of products also. These relationships are of great importance in calculations of thermal efficiencies of heating operations and necessitate much laborious arithmetical work. This can, however, be obviated by suitable graphical treatment. G. B. Howarth[75] has developed a graphical method applicable to fuels of all compositions which minimises the number of experimental measurements necessary. A determination of carbon dioxide, given a knowledge of the composition of the fuel, enables one to infer the percentage of oxygen in the flue gas and the proportion of excess air. By means of other diagrams the heat capacity of the products of combustion and the theoretical temperature of combustion can be read off. Considerable developments of graphical methods of treating fuel calculations have also been made by Wa. Ostwald. His use of the Gibbs system of triangular co-ordinates[76] for the graphical representation of producer-gas composition is interesting and suggestive. This treatment has been applied also by F. Schulte[77] to the graphical calculation of the flue gases of coals.

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[70] *Cf.* Morgan, "Principles of Spark Ignition," London, 1920; also Paterson and Campbell, *Proc. Phys. Soc.*, 1919, **31**, 193.

[71] *Chem. Soc. Trans.*, 1917, **111**, 1003; *J.*, 1917, 1264.

[72] *Chem. Soc. Trans.*, 1919, **115**, 1248; *J.*, 1920, 54A.

[73] *Gas World*, 1920, **73**, 387, 407; *J.*, 1920, 812A.

[74] *Gas J.*, 1920, **152**, 459.

[75] *J.*, 1920, 329T.

[76] *J.*, 1919, 492A.

W. T. David[78] has examined photographically the connexion between radiation and pressure of explosion of mixtures of coal gas and hydrogen with air with a view to ascertaining the conditions governing emission of radiation during explosion. This is important in its bearing on the working of internal combustion engines.

CHEMISTRY OF COAL.

As indicated earlier, the pursuit of this branch of chemistry is being carried on with increasing energy in many quarters. Work on carbonisation is dealt with more particularly in the section on "Gas" (p. 42).

Further observations have been recorded on the properties of the four constituents of banded bituminous coal identified by Marie C. Stopes.[79] This method of measuring the properties of the constituents of coal separately seems to promise more than the study of the mixed bulked samples as hitherto commonly made. R. Lessing[80] has recorded the results of carbonisation tests on the four components of Hamstead coal in the small apparatus designed by him. Fusain had no coking properties at all, and with durain coking was but slightly more marked. Clarain gave a more coherent coke and vitrain the most coherent of all. The difference in the yields of products seemed to indicate variation in the character of the primary decomposition products. He further examined the differences between the ash obtained from the four constituents. Fusain was distinguished by a more variable and much higher ash content (mainly lime) than the other constituents; durain ash contained alumina and silica almost in the proportions of kaolinite. The ashes of clarain and vitrain were both mainly soluble in dilute hydrochloric acid and were possibly residues of plant ashes. These results leave much ground for speculation and the author believes that the "refining" of coal by washing is still in a crude state on account of lack of knowledge as to the distribution of the ash.

F. V. Tideswell and R. V. Wheeler[81] have measured the rate of oxidation of the four proximate constituents of Stopes. Obviously this might at first sight be expected to give more insight into the process of spontaneous combustion than measurements made on bulk samples. The differences actually observed were not sufficient to permit of conclusions as to which constituent is responsible for spontaneous combustion. Although fusain absorbed oxygen more readily at low temperatures, this position was not maintained at higher temperatures, when vitrain seemed to be the most inflammable constituent.

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[77] *Glückauf*, 1920, **56**, 532; *J.*, 1920, 812A.

[78] *Phil. Mag.*, 1920, **39**, 66, 84; *J.*, 1920, 218A, 219A. *Proc. Roy. Soc.*, 1920, A, **98**, 183; *J.*, 1920, 812A.

[79] *Proc. Roy. Soc.*, 1919, B, **90**, 470; *J.*, 1919, 452A.

[80] *Chem. Soc. Trans.*, 1920, **117**, 247, 256; *J.*, 1920, 356A.

[81] *Chem. Soc. Trans.*, 1920, **117**, 794; *J.*, 1920, 591A.

E. Sinkinson[82] has attempted, although inconclusively, to identify the constituent of coal which is responsible for its well known action on a photographic plate. Carbonisation at 500°–550° C. suffices to destroy the active constituent which occurs in the pyridine extract. The presence of oxygen seems essential to the production of the photographic effect.

The same observer[83] reports a very interesting attempt to follow the carbonisation process by measurements of the electrical conductivity of the coke product. Whereas raw coal is an insulator, coke has marked conducting power, presumed to be due to free graphitic carbon. It was found that the resistance of coal and also of cellulose broke down at temperatures round about 500° C., presumably due to the liberation of sufficient free carbon to form a conducting bridge, and at higher temperatures the conductivity rose rapidly. Only five coals, one of which was non-coking, were tested. The results are insufficient to allow of generalising, but it is perhaps significant that the lowest figure (450°) was found with the non-coking coal.

R. Kempf[84] records a hysteresis effect in the evolution of the moisture of coal. The moisture content of the coal in apparent equilibrium with the atmosphere depended on previous treatment, so that it is insufficient to describe a sample as " air dried " ; the actual moisture content should be stated.

Under the auspices of the Lancashire and Cheshire Coal Research Association, F. S. Sinnatt is studying the properties of the local coals, issuing results in the form of convenient bulletins. F. S. Sinnatt and A. Grounds[85] have studied the well known caking test, originally suggested by Campredon. J. T. Dunn[86] criticised the use of sand as inert material owing to the possibility of reaction with ash constituents and suggested anthracite as preferable. The authors have made a much more comprehensive study in which electrode carbon crushed to powders of varying fineness was used. Grain size had an enormous effect on the apparent caking power and the curve connecting agglutinating power with grain size was found to be a characteristic of a given coal. Clearly the test is one requiring the most careful standardisation to obtain even comparative figures, while it is doubtful if absolute values will be attainable. The known deleterious influence of fine washery slurry on the coking of coal in ovens is also evident from these results. It is also suggested that the admixture of fines might be advantageously employed to render excessively caking coals more suitable for steaming. F. S. Sinnatt and B. Moore[87] have described experiments to determine the relative ignition temperatures of finely divided coal using an apparatus similar to that of H. Moore.[88] They found that at certain temperatures coals would glow, but were reluctant to ignite with visible flame. These temperatures they believed coincided with the evolution of volatile matter which extinguished flame by exceeding the limits of inflammability. Coals known to be liable to spontaneous ignition did not show this peculiarity. F. S. Sinnatt, H. Stern, and F. Bayley[89] report that the material taken from the dust collector of a belt picking room contained 49% of fusain which ignites with considerable ease at a low temperature and may promote the firing of coal.

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[82] *Chem. Soc. Trans.*, 1920, **117**, 165 ; *J.*, 1920, 357A.

[83] *Chem. Soc. Trans.*, 1920, **117**, 839 ; *J.*, 1920, 591A.

[84] *Mitt. K. Materialprüf.*, 1920, **37**, 178 ; *J.*, 1920, 620A.

[85] *J.*, 1920, 83T.

[86] *J.*, 1913, 397.

The shortcomings of the Kjeldahl process have been emphasized again by A. Parker,[90] who found it impossible to establish a nitrogen balance sheet in carbonisation tests until he applied a modified Dumas method.[91]

F. Fischer[92] states that the Eschka method yields results much too ow when the percentage of sulphur in coal is high. He reports a ase in which 7·7% was found as against 9·8% in a sealed tube.

A. R. Powell and S. W. Parr[93] believe that the sulphur content f coal is of four types, "resinic organic," soluble in phenol, "humus rganic," pyritic and sulphate, and have devised methods for letermining the relative proportions of these. They have studied he behaviour of the four types in carbonisation. The resinic and ome of the humus sulphur is believed to be retained by the coke.

A. R. Powell[94] has studied the behaviour of the different kinds f sulphur in coal carbonised alone or in a current of hydrogen. Vithout hydrogen both pyrites and sulphates are converted into ulphides and the proportion of the sulphur in organic combination nay increase. In presence of hydrogen at 1000° C. practically all he sulphur is removed as hydrogen sulphide which suggests the ossibility of reducing the sulphur content of coke by suitable reatment. The effect of diluted hydrogen such as coal gas is imilar though less pronounced, and these reactions play an important part in carbonisation. No carbon bisulphide was formed in any test at low temperatures, and it is inferred that when present in coal gas it is a secondary product of reaction between carbon and hydrogen sulphide.

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[87] *J.*, 1920, 72T. *Cf.* Wheeler, *Chem. Soc. Trans.*, 1918, **113**, 945.

[88] *J.*, 1917, 109.

[89] *Bull.* 5, *Lancs. and Cheshire Coal Research Assoc.*, 1920; *J.*, 1920, 438A

[90] *Gas J.*, 1920, **150**, 604; *J.*, 1920, 507A.

[91] See *J.*, 1919, 399A; *Ann. Repts.*, 1919, **4**, 579.

[92] *Ges. Abhandl. zur Kenntnis der Kohle*, 1918, **3**, 98; *J.*, 1920, 146A.

[93] *Bull. Eng. Expt. Stat. Illinois Univ.*; *Gas J.*, 1920, **149**, 79; *J.*, 1920, 15A.

[94] *J. Ind. Eng. Chem.*, 1920, **12**, 1069, 1077; *J.*, 1920, 811A.

Another interesting note on the pyrites in American coal, by H. F. Yancey,[95] contains the suggestion that at least 1,500,000 tons of pyrites concentrates could be recovered, and that these would usually be suitable for use in sulphuric acid manufacture. Low in arsenic and phosphorus, much of the burnt cinder could be sent to the blast furnace.

The focussing of attention on the minor constituents of coal is to be welcomed. There is a large quantity of coal in this country, often of high fuel value, which is undesirably rich in sulphur. This at once limits its sphere of usefulness. For carbonisation, either in coke ovens or gasworks, it is impossible to use the coal which may, however, give excellent yields of by-products. Even when used for ordinary fuel purposes, it is undesirable to turn such quantities of oxides of sulphur into the atmosphere. The sulphur, unfortunately, is often mainly organic, and washing is ineffective. The rational treatment of these coals must be regarded as an unsolved and urgent problem of fuel technology.

A. L. Booth[96] advocates the selection of coal for fuel purposes in accordance with the observations on transparent sections under the microscope. Chemical classification fails to distinguish between coals of essentially different character, viz., (A) humic coals from the leaves and woody tissues suitable for steam raising, (B) spore coals for producer work. Cannels differ widely from these and are suitable for reverberatory furnaces. The microscope is, it is claimed, a sure guide to the suitability of a coal for varying technical purposes.

[95] *Chem. and Met. Eng.*, 1920, **22**, 105 ; *J.*, 1920, 187A.

[96] *J. Iron and Steel Inst.*, 1920, **52**, 271 ; *J.*, 1920, 683A.

GAS—DESTRUCTIVE DISTILLATION—TAR PRODUCTS.

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The progress of applied chemistry in the carbonising industries has been greatly hampered by delays in the supply of plant, and by general labour difficulties. Often the application of a new principle has been delayed by the impossibility of getting plant or labour until the seasonal or economic situation had changed for the worse. Many new ideas, developed as far as possible, await more favourable industrial conditions before being placed on a large-scale basis. Reconstruction has been similarly handicapped owing to skilled labour being required in many other directions.

Although the hopes of the gas industry for better financial conditions may in part be realised at the end of the year, the impetus which such should give to development is not yet to be seen. The supply of the chief raw material, coal, has been so uncertain that selection of coal suitable for any particular purpose has been practically impossible. A very great economy could be effected if the various coals could be restricted to those uses for which they are particularly suited.

Many of the problems of the gas chemist will never be realised until the constitution of coal has been revealed. The investigation of different methods of carbonisation and comparison of results begins to reveal valuable information in this respect, and any new work is worthy of study by those undertaking research into this question.

In reviewing the year the general economic conditions must be kept closely in mind. In no previous year has this been more necessary; for the high prices of coke and other by-products has exerted a far-reaching effect on the processes favoured.

The economics of the gas industry particularly in relation to electric supply has been the subject of many reviews. While this aspect is treated from a general standpoint in the section on "Fuel," it will be useful to discuss the particular efficiency figures of the gas and coke industries. A clear statement of the general efficiency of gasworks' practice with discussion of future possibilities is given by Sir Dugald Clerk[1] and may be taken as closely representing the by-product industry. The best practice of carbonisation for production of straight coal-gas gives the following supply of heat in the various forms :—

As coal gas	25
As coke	54
As tar	6
	—
Total	85
Heat used and lost	15
	—
Heat of original coal	100

In addition allowance should be made for products recovered of which none or only part can be reckoned on a thermal basis. If the whole of the heat lost be debited against the gas the thermal efficiency of gas production is in the best case 62·5%, but on the average efficiency throughout the country only 46%. By the introduction of water-gas the total heat of the gas has been raised to 30% but as water-gas generation is less efficient (58%) the total thermal efficiency is reduced.

The Final Report of the Nitrogen Products Committee[2] also presents a thermal balance sheet of gas and coke oven practice in which the general efficiency of the carbonising plant is given as 73·7% rising on occasion to over 82%. Naturally the tendency to convert more and more of the energy of the solid coal into gaseous form makes it more difficult to improve on these figures. Extremely interesting figures are given in respect to power production on a large scale from different systems, with estimates of capital and operating costs, and revenue from by-products. These briefly show that the by-product system can hardly compete with direct-fired systems for large-scale power production, although much depends on the ratio of the values of the by-products to that of the coal. It is important not to lose sight of the fact that the value of the by-products allowed is mostly the value of the crude products as delivered from the carbonising plants, but as these raw materials are worked up into a large number of commodities of increasing value, the total gain would be considerably more than represented.

In a very important paper, E. G. Stewart[3] gives similar figures for the efficiency of modern gas manufacture. He finds that 66% of the heat value of the coal appears in the coke. Of this 16% is used as fuel, which is made up of 8·6% passing to the retorts, 3·4% lost through radiation and in the ashes, and 4% leaving as sensible heat in the flue gases. Of the heat given to the retort, 3% is involved in carbonisation, 2·3% is carried away by the gases leaving and

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[1] *Gas J.*, 1920, **150**, 479 ; *J.*, 1920, 357A

[2] *M. Mun. Inv. Dept.*, 1920, 171.

[3] *Gas J.*, 1920, **149**, 750 ; *J.*, 1920, 357A

3·3% in the hot coke leaving. Consideration will show that these losses may be somewhat reduced. The heat carried away in the coal-gas may be in part recovered by using water-cooled condensers and feeding the hot water to the boilers. The heat in the coke leaving is appreciably diminished in vertical retort systems where it is used for preheating the primary and secondary air. The heat in the waste gases is often brought to a low figure by regeneration. The reduction of losses by radiation has been given some attention, as the better working conditions on the newer retort houses bear witness. The use of better conducting materials with consequent lower combustion flue temperatures tends to reduce such losses. In this connexion papers by K. Bunte[4] and G. Dougill[5] are very suggestive.

It is interesting to note that the Joint Sub-Committee of the Institution of Gas Engineers and the University of Leeds have obtained new figures for the heat of decomposition of coal by carbonisation. They found an average heat absorption of 1·8% confirming Barnum's results, and in opposition to those of Euchene, and concluded that the heat of decomposition of the coal used in the tests was certainly very small, and probably negative in sign.

Steaming.—Steaming in vertical retorts has received a good deal of attention. The extensive and detailed results of the trials carried out by the Joint Research Sub-Committee of the Institution of Gas Engineers and the University of Leeds,[6] should be studied in the original. Generally speaking, there seems to be a limit to which steaming can be profitably carried, and naturally it is a question of deciding this limit according to the coal used and conditions, which vary from place to place and from time to time. The Report provides a firm basis on which to work and is an excellent example of a large-scale trial. The coal used was 1-in. washed nuts of a semi-caking variety. The steam used ranged from nil to 50% in five comparative tests, in which the steam was increased by approximately 12% in each case. Taking the results on the dry basis, the gas made varied between 10,384 to 21,849 cb.ft. per ton at the two limits, and the calorific value from 544 B.Th.U. gross to 410 B.Th.U. gross. The total heat in the gas, therefore, increased from 5·649 million B.Th.U. to 8·958 million B.Th.U. The total heat contents of the products available for sale was gradually reduced from 83·18 to 77·92%. The efficiency of gas production reached a maximum of 62·09% in the fourth test where the total yield of gas was 19,902 cb.ft. per ton, while the efficiency of carbonisation fell below 80% only in the fifth extreme case to 77·92%. The yield of coke fell from 13·28 cwt. to 11·52 cwt. The quality of the extra gas made due to steaming was calculated and the value is shown to have dropped from 342 to 274 B.Th.U. gross. It is interesting to note that the percentage of olefinic hydrocarbons was maintained in this extra gas, even at the extreme limit of steaming, but the methane fell away. The additional amount of carbon dioxide formed presents a serious drawback to extensive steaming. The hydrogen sulphide decreased on a percentage basis but increased in total volume. The yield of cyanogen in the gas and liquor was almost constant. Calculated as pure ammonium sulphate the total yield of ammonia rose from 36·3 to 43·9 lb. per ton. The coke varied little in appearance and physical properties and the volatile matter was practically the same—an observation which supports the idea that steam does not materially help in driving out the volatile matter, but effects conservation by diluting the hydrocarbons and removing them from deleterious influences. The ash rose from 10·1 to 15·1% on the reduced yield of coke. Tar (dry) increased from 14·6 to 23·7 gallons per ton and contained an increasing amount of soft pitch, but less free carbon. An interesting attempt was made at complete gasification.

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[4] *J. Gasbeleucht.*, 1920; *Gas J.*, 1920, **152**, 389.

[5] *Gas J.*, 1920, **152**, 454.

[6] 4th Report; *Gas J.*, 1920, **150**, 604; *J.*, 1920, 507A.

C. F. Tooby[7] regards steaming in vertical retorts as a step towards complete gasification, although it might not be advisable to gasify the whole of the coke in this way. It would appear that the extra gas can be made more cheaply than by generating water-gas separately, unless losses during the "blow" are minimised in some way. It is pointed out that in vertical retorts there must be a reduction in the rate of coal throughput when steaming compared with the maximum rate without steaming. High bottom heats are advocated as a means of reducing this disadvantage. Comparison is made between complete gasification in Mond producers and verticals without steaming, and also when the coke from the latter is converted into water-gas in a separate generator.

H. Strache[8] advocates primary carbonisation followed by extensive steaming, and claims a greater yield of by-products and a larger yield of heat units in the gas than would result from separate generation of the water-gas.

Considerable trouble has been experienced in the reduction of the heats and undue consumption of steam when wet steam has been used. To overcome this difficulty the steam has been superheated by passage through tubes inserted in the waste gas circulating flues of the Glover-West system, or even by building in the tubes in the walls of the setting, so that the steam may enter the retorts in a highly superheated condition.[9]

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[7] *Gas J.*, 1920, **149**, 502.

[8] *J. Gasbeleucht.*, 1920, **63**, 230; *J.*, 1920, 477A.

The use of steam is naturally conditioned by the heats being maintained, and the carbon dioxide content of the crude gas has been found to provide a good indication that this is so.

Steaming in horizontal retorts has not found the same convenience of application.

Vertical Retorts.

Difficulties experienced in carbonising Durham coals have given rise to the impression that such are unsuitable for vertical plants, chiefly owing to the reduced daily makes. T. Hardie and C. Dru Drury[10] agree that while Durham coal requires somewhat different and more strenuous treatment, there is no difficulty in using it provided that the heats are maintained. G. Weyman[11] points out that the coals from the Durham area are of many different types; some of these require more heating than others to coke them. The vertical retort is very discriminating in this respect, as the variation in rate of carbonisation is easily seen and appreciated. By selection of coals the capacity of a continuous vertical plant may be increased 25–30%. A method for determining this factor experimentally is described.

It is interesting to find that both at home and abroad attempts have been made to use coal gas for heating retort settings by turning the gas direct into the producer-gas flues, and shutting down the producer. The chief trouble appears to have been due to imperfect mixing of gas and air in the combustion flues which were designed to take mixtures of producer-gas and air. The application of a suitable burner would no doubt overcome this difficulty.

Horizontal Retorts.

Progress has been made in these installations by more general introduction of retort house governors followed in many cases by the use of dry mains.

The interesting research of S. F. Dufton and J. W. Cobb[12] on the high-temperature reactions of benzene and toluene forms an extension of the previous work of the Gas Research Fellow at the University of Leeds, dealing with the influence of red-hot coke on the products of carbonisation. In the work now described a gas either of an inert character, such as nitrogen, or active, such as hydrogen, was saturated with pure benzene or toluene and passed through coke at various temperatures. With a time of contact of 12 secs. in inert gas, benzene began to form condensation products at 500° C., the first being diphenyl. At 750° C. more complex saturated compounds formed and at 920° C. free carbon appeared in quantity. The formation of diphenyl is reversible. In presence of hydrogen benzene is stable at 800° C. Toluene is subject to condensation in an inert gas at 550° C., one product being stilbene. At 750° C. naphthalene, diphenyl, anthracene, and soft pitch formed. When hydrogen was present condensation was delayed and toluene reduced to benzene and methane. Xylene and cresol in the presence of hydrogen yielded toluene and benzene.[13]

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[9] Woodall, Duckham, and Jones, and A. M. Duckham, E.P. 150,589; *Gas J.*, 1920, **152**, 34; *J.*, 1920, 715A.

[10] *Gas J.*, 1920, **150**, 260, 266.

[11] *J.*, 1920, 168T.

[12] *Gas J.*, 1920, **150**, 588; *J.*, 1920, 511A.

From the amount of phenolic substances found in low temperature tar and the fact that phenols are easily reduced by hydrogen to toluene, and the toluene to benzene and methane, it seems probable that the benzenoid hydrocarbons are derived from the oxygenated compounds of the coal.

Complete Gasification.

Complete gasification is finding many advocates[14] as a source of cheap heat, light, and power, and with increasing scarcity of oil becomes a more useful proposition than carburetted water-gas manufacture. Results from the plants at Grantham, Normanton, Sheffield, and Bolton will be awaited with interest. Such plants might be very useful in supplementing and forming a standby to town supply from coke ovens.

Combined plants in which the coal is first carbonised and then completely gasified have drawn much attention and possess the advantage that by-products are recovered. The system of H. Strache[15] consists of a vertical retort superimposed on a producer. The producer is worked up to incandescence by a blast, and the blast gases passed up through heating flues arranged around the retort to a superheater which heats up the large amount of steam used. On turning this steam to the producer the exits to the heating flues are checked and the water-gas passing to the retort helps in carbonising the coal. Arrangements are also made for taking off the water-gas prior to passing into the retort and treating it separately from the coal gas. Other plants after the same style have been projected.[16] At Harrogate, combined gasification has been obtained by pushing the hot coke from horizontal settings into a water-gas generator situated at a lower level. During the blast the generator gas is used to heat the retorts while during the run the hot blue gas passes through the retort. The effect is similar to that obtained by carbonising the coal at fairly low temperatures, and the tar is very fluid. A yield of 60,000 cb. ft. of gas of 325 B.Th.U. gross at the rate of 200,000 cb. ft. per 24 hrs. is recorded.[17]

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[13] See Young Memorial Lecture, *Gas J.*, 1918, **143**, 482; *Ann. Repts.*, 1918, **47**, 49; and F. Fischer and H. Schrader, *Brennstoff-Chem.*, 1920, **1**, 4, 22; *J.*, 1920, 740A.

[14] *Times, Eng. Suppl.*, 1920, March; *J.*, 1920, 124R.

[15] E.P. 117,083; *J.*, 1920, 439A.

[16] C. F. Broadhead, E.P. 122,179; *J.*, 1920, 395A.

In a most interesting paper H. J. Hodsman and J. W. Cobb review the possibilities involved were a cheap supply of oxygen available in large quantities. The heating of retorts could be made internal and the bad conductivity of retort materials and the high heats necessary in the combustion flues could be avoided. The process of carbonisation could be carried to complete gasification or restricted to partial gasification with great ease. An efficiency of 90% is considered possible for complete gasification.[18] The question is of particular interest in France and Switzerland, where water power is sufficient for a large-scale generation of power for separating the oxygen from the atmosphere.[19]

Low Temperature Carbonisation.

The possibilities of this method of carbonisation are being slowly developed on medium size plants. C. D. Burney prefers internal heating,[20] and passes hot furnace gases through the hollow parts of a screw or mechanical arrangement which functions both as a heat distributor and as a means of moving the charge through the retort. Provision is made for drawing off the products from different parts of the retort and condensing separately. The tunnel oven is also proposed for this purpose, in which the material is passed through the horizontal retort in trucks. Transverse walls project downwards at intervals just sufficiently to allow clearance for the trucks. Distillates are withdrawn from the pockets so formed, thus effecting a fractional distillation.[21]

Troubles in connexion with drawing the charge at an even rate through the retort similar to those experienced in the earlier vertical retort high-temperature systems, have led to several attempts to destroy the caking power of the coal by slow preheating prior to introduction to the retort proper,[22] an expedient also put forward as a preliminary treatment for coal to be used subsequently in a producer.[23]

H. K. Benson and R. E. Canfield[24] describe the result of carbonising an inferior coal of a type common in this country. Yields of gas and compositions are given for different carbonising temperatures. A well-defined decomposition point was found between 350° and 400° C., which marked a maximum in the yield of tar oil and an abrupt rise in the quantity of methane and hydrogen evolved. The maximum amount of raw oil was about 3·5% of the weight of the coal.

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[17] *Gas J.*, 1920, **152**, 283.

[18] *Gas J.*, 1920, **150**, 640 ; *J.*, 1920, 508A.

[19] M. Zollikofer, *Gas J.*, 1920, **152**, 30.

[20] E.P. 136,585 ; *J.*, 1920, 149A.

[21] C. Dressler, E.P. 149,086 ; *J.*, 1920, 652A.

[22] G.P. 301,602 ; *J.*, 1920, 149A ; E.P. 136,868.

[23] E.P. 123,738 ; *J.*, 1920, 478A.

[24] *J. Ind. Eng. Chem.*, 1920, **12**, 443 ; *J.*, 1920, 438A.

The semi-coke resulting in most cases does not seem to have proved of domestic utility, and the tendency is to use up the carbonaceous residue by briquetting for use in producers or for carbonising at high temperature in retorts. E. Roser[25] carbonises the coal in a rotary kiln at a low temperature, collects the tar and oils, briquettes the semi-coke and uses it in a producer. He considers that the heating value of the gas obtained is only one-sixth less than the heat obtained when the same coal is used direct in a producer, and the yield of tar oils more than compensates for this difference. F. Fischer and W. Gluud[26] found in one specimen of semi-coke 1·9% of nitrogen on the ash-free basis, corresponding to two-thirds of the nitrogen of the original coal. When heated above 575° C. it gave up one third of the nitrogen as ammonia, while in a current of steam almost the whole was so liberated. The distribution of the nitrogen in the process is examined by W. Gluud and P. K. Breuer.[27] The only serious shortcoming of the semi-coke as a fuel was its friability. The use of the residue as a fuel suspended in oil or in a powdered condition may make a very considerable difference to low-temperature processes. An extreme case of low-temperature work is provided by a system in which distillation is effected at 200°–300° C. by metallic electrical resistance heaters which subdivide the charge. The process takes 20 hrs., and gives a liquid product resembling petroleum.[28] A. E. Beet and A. E. Findley propose to separate coking slack into three grades by flotation, using the middle grade for low-temperature use. This grade, which is 17–34% of the whole, would yield a semi-coke with 7–12% of ash, 6–10% of volatile matter, and 20–25 gallons of oil per ton with 11–15 lb. of sulphate of ammonia and 7000 cb. ft. of rich gas.[29]

A satisfactory yield of ammonia does not seem to be possible unless the semi-coke is subjected to a higher temperature. Steaming during carbonisation does not help in this respect.[30]

COKE OVENS.

The use of by-product coke-ovens is steadily increasing. The Nitrogen Products Committee's Report already referred to gives two-thirds of the coal as being carbonised in such ovens in this country, while in America the number of by-product ovens exceeded that of beehive ovens in 1919.

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[25] *Stahl u. Eisen*, 1920, **40**, 741 ; *J.*, 1920, 508A.
[26] *Chem. Zentr.*, 1919, **90**, IV., 880 ; *J.*, 1920, 93A, 218A.
[27] *Chem. Zentr.*, 1919, **90**, IV., 1066 ; *J.*, 1920, 259A.
[28] E.P. 137,572 ; *J.*, 1920, 222A.
[29] *Gas J.*, 1920, **151**, 670.
[30] *Z. f. Dampfkessel*, 1920.

The Conference on By-Product Coking held at the Annual Meeting of the Society at Newcastle-upon-Tyne during the year under review was both interesting and important.[31]

A. H. Middleton[32] finds that if the flueless space at the top of coke ovens is increased paraffinoid hydrocarbons appear in the recovered benzol, the quality of which therefore diminishes. Ammonia recovery tends to increase. When smaller charges were introduced the paraffins disappeared. By maintaining the heats well to the top and again charging full, satisfactory conditions were obtained. These results may be contrasted with similar phenomena found in gasworks practice.

The shorter time required for coke ovens of the same width in America to work off a charge compared with British plants (about 60%) is considered by J. I. Thompson[33] to be due to the more extensive use of silica brick in America and consequent employment of higher heats with better conductivity. J. Enzenauer[34] comparing the silica brick ($SiO_2=95\%$), and fireclay brick ($SiO_2=80\%$) finds that the former gives a coking period of 5 hrs. less and after 4–5 years' use it is in better condition, having suffered less from corrosion and erosion. The use of silica brick, it is pointed out, might lead to the recovery of smaller yields of by-products owing to the tendency to employ higher temperatures. In gasworks both at home and abroad satisfaction has been obtained with composite settings built up of fireclay where the wear and tear is great, and silica brick in the middle where the maximum transference of heat is required. In this respect the views of W. H. Fulweiler and J. H. Taussig should be consulted.[35]

The question of heating coke ovens with producer gas has been been the subject of consideration. T. B. Smith[36] recommends inferior coal producers with ammonia recovery and gives a favourable balance sheet. J. Becker and F. W. Sperr[37] recommend this system of heating as being capable of more easy adjustment and giving more uniform heating.

Attention is again called by W. J. Rees[38] to the corrosion of coke oven walls by salt. It is found that the action is more severe on fireclay than on the more silicious materials.

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[31] *J.*, 1920, 194T *seq.*, 248R.

[32] *Gas World*, 1920, **72**, *Coking Sect.*, Jan 3rd, 13 ; *J.*, 1920, 94A.

[33] *Gas World*, 1920, **72**, *Coking Sect.*, May 1st, 14.

[34] *Glückauf*, 1920, **56**, 785 ; *J.*, 1920, 713A.

[35] *J. Ind. Eng. Chem.*, 1919, **11**, 1153 ; *J.*, 1920, 93A.

[36] *Gas World*, 1920, **72**, *Coking Sect.*, Jan. 3rd, 10.

[37] *Gas World*, 1920, **73**, *Coking Sect.*, Sept. 4th, 10.

[38] *J.*, 1920, 197T ; *Gas World*, 1920, **72**, *Coking Sect.*, June 5th, 9 ; *J.*, 1920, 217A.

W. A. Ward[39] gives an extensive and detailed paper on coke oven construction, which should be consulted by those concerned with the design of new installations.

The practice of adding large amounts of water to the coal as charged is being considerably modified and meets with condemnation by H. Thwaite[40] and E. W. Smith.[41] Any advantages derived from the presence of steam driven off from this water are not sufficient to counterbalance the disadvantages of the extra heat required to expel it, the effect on the walls, and the strain on exhausters, condensers, and other plant. H. Thwaite considers that an extra carbonising period of two hours is required for every 2% of moisture over 10% and recommends as the optimum 8–10%.

G. Hinselmann[42] applies steaming to coke ovens by passing steam into the nearly coked ovens and using the water-gas so generated to help in transferring heat to newly charged ovens.

The work of S. R. Illingworth[43] is most important. Four coals were examined comparatively and the results obtained justify the hope that much progress will be made by such study. Coking property is ascribed solely to the resinic portion, and this portion of the coal suffers progressive destruction at 450° C. Experiments to find the amount of resinic matter which must be left in order to produce a coherent residue show that there is a difference in the cementing power of the resinic portions of the four coals examined. The author considers that the plasticity of coal on heating is due to the liquation of the resins which melt at 200° C. and are fluid at 350° C. As the temperature is raised the resins decompose, leaving a skeleton of carbon around the non-melting constituents. The subsequent properties of the coke not only depend on the amount and properties of the resins but also on the parallel decomposition of the β-cellulosic constituents during the crucial period when the resins have reached their fluid condition and are decomposing. A strong evolution of gas at the critical period produces a less dense coke. E. Sinkinson[44] suggests that the formation of free carbon which provides an electrical conductivity and takes place at about 500° C. is due to the decomposition of the cellulosic constituents, since cellulose itself undergoes a similar change.

F. S. Sinnatt and A. Grounds[45] find that the caking power of Lancashire coals varies considerably. Work in connexion with the "agglutinating power" of coal led to the observation that of higher sulphides is brought about. On oxidation in presence of steam ferrous sulphate results. This may be decomposed by ammonia and the ammonium sulphate removed in solution and crystallised. On a small scale, using the waste gases from a sulphate of ammonia plant, 30% of the spent oxide was removed as ferrous sulphate.

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[39] *J.*, 1920, 198T.

[40] *Gas World*, 1920, 72, *Coking Sect.*, Apr. 3rd, 38 ; *J.*, 1920, 357A.

[41] *J.*, 1920, 194T.

[42] G.P. 319,246 ; *J.*, 1920, 439A.

[43] *J.*, 1920, 111T, 133T.

[44] *Chem. Soc. Trans.*, 1920, 117, 839 ; *J.*, 1920, 591A

[45] *J.*, 1920, 83T.

In revivifying oxide in the boxes when the box has been shut off from the main gas stream, O. B. Evans[53] prefers to draw air through under a slight suction to avoid local heating.

W. J. Dibdin applies a well-known reaction,

$$3S+2H_2O=2H_2S+SO_2,$$

to drive off sulphur from spent oxide by heating the latter in a current of superheated steam. On condensation the sulphur is again deposited by the reverse reaction.[54]

As a result of negotiation between the purchasers of spent oxide and the National Gas Council, the Marsden sulphuric acid method has been adopted as a standard method for estimating sulphur in spent oxide. Methods of sampling were also agreed upon.[55]

In the removal of carbon bisulphide the Carpenter-Evans process still remains the only method used on a large scale. A patent[56] of J. H. Corthesy and S. T. S. Castelli proposes to replace the nickel catalyst by granulated alumina or high-grade bauxite. It is possible that this catalyst may be affected by the burning off of the carbon. In considering the removal of carbon bisulphide the process of O. Guillet,[57] which uses the reaction,

$$CS_2+2H_2O=2H_2S+CO_2,$$

should not be lost sight of. The catalyst removes the hydrogen sulphide already present in the gas, as well as that formed in the reaction. Owing to the heat liberated by absorption and oxidation of the hydrogen sulphide the process is nearly self-supporting. This process probably accounts for the observation of G. Weyman[58] that oxide purifiers may remove an appreciable portion of the carbon bisulphide. In the Rideal-Taylor process a compound catalyst is employed which is not allowed to absorb the hydrogen sulphide formed.[59] This necessitates external heating of the gas and catalyst, and provision of plant for the removal of the trace of hydrogen sulphide formed.

Carbon bisulphide is also removed by oil-washing for benzol. The extent of the removal is normally about 7 to 10 grains per

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[53] *Gas J.*, 1919, **148**, 726 ; *J.*, 1920, 96A.
[54] E.P. 141,172 ; *J.*, 1920, 440A.
[55] *Gas J.*, 1920, **150**, 141 ; *J.*, 1920, 402A.
[56] E.P. 143,641 ; *J.*, 1920, 510A.
[57] E.P. 18,597, 1913 ; *Ann. Repts.*, 1916, **1**, 48
[58] *loc. cit.*
[59] *Ann. Repts.*, 1919, **4**, 54.

100 cb. ft. on gas carrying 25 grains per 100 cb. ft. E. R. Hamilton[60] proposes to use this method for reducing the very high sulphur content of the gas from Nova Scotian coals. From 0·5 to 1 gallon of paraffin oil per 1,000 cb. ft. is to be used in a set of steel towers, 4 ft. diam. and 16 ft. high, packed with grids.

AMMONIA.

Statistics of the production of ammonia and its compounds compiled from the Ministry of Munitions returns made for 1918 are presented by D. V. Hollingworth and E. J. Fottrell.[61] Calculated at 25% sulphate of ammonia the average yield from gas concerns was 22·42 lb. per ton of coal carbonised. The average yield of individual works was only 18·4 lb. per ton, which gives an indication of the losses which must be occurring in the smaller works, particularly when account is taken of the fact that if the crude liquor is sold as such the returns are based on the total content and do not include the losses sustained in the subsequent working up. Besides working their liquor up to sulphate, many of the larger works make concentrated liquor or use ammonia as a reagent, when larger losses would naturally be expected to occur. The number of works recovering less than 20 lb. per ton is more than half the total and responsible for five million tons of wet coal. The huge losses in the smaller works are considered to be due to disregard of yields, losses by evaporation during transference and storage, and loss in the spent liquor when sulphate is made. At the beginning of 1918 no less than 336 gasworks carbonising 135,000 tons of coal per annum were wasting the whole of the liquor produced. Most of these would be situated in country districts, and one would suppose that some trial might have been made of direct application of the liquor as a fumigant and manure after suitable dilution.[62]

The recovery from coke ovens is distinctly higher, and in 116 installations the average yield is given as 26·1 lb. with an average individual yield of 27·1 lb. That the latter figure is higher is ascribed to the low nitrogen content of many of the coke-oven coals. Only seven works recovered less than 20 lb.

These figures may be compared with producer-gas plants where the average recovery of 25 works was about 61 lb. Two of these recovered over 100 lb. per ton of dry coal; at one of these slaked lime was added to the charge.

The recovery in 1920 in gas works has been helped by the prevalence of "steaming," but it is possible that losses have been somewhat increased by the lower strength of the liquor made. In one works it is estimated that moderate steaming corresponding to a make of about 15,000 cb. ft. per ton led to an increased recovery of just over one lb. of sulphate per ton, although there is no doubt that the steaming was responsible for an increased yield of ammonia as liquor of a good deal more than the equivalent of this. Naturally additional benefit depends largely on the coal used.

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[60] *Gas J.*, 1920, **152**, 333.

[61] *Gas J.*, 1920, **149**, 557.

[62] *Gas J.*, 1919, **148**, 653.

The direct process in gasworks has not made much headway, but the Alkali Inspector reports a distinct improvement in the recovery at those works where the plants were under strict chemical supervision.[63]

W. S. Curphey[64] seeks to eliminate impurity in the salt from the direct process, particularly where "Burkheiser" salt is made, by dividing the saturation of the acid into two stages. The gas used to combine with the acid in the first stage contains little ammonia and much impurity. The partially saturated acid, which may contain sulphur from the interaction of hydrogen sulphide and sulphurous acid or sulphur dioxide in the first stage, may then be cleaned up by filtration or other means before submitting it to final saturation with nearly pure ammonia gas. The separation of the two types of gases containing ammonia is effected in a similar manner to that used in concentrated liquor manufacture.

Much work and many patents have resulted from attempts to utilise nitre cake with or without adding fresh acid, but it hardly seems likely that the processes involved will remain in use in view of the altered circumstances.

In the process for absorbing ammonia in sodium bisulphate solution it is claimed that a double salt is precipitated which may be decomposed with evolution of the ammonia by heating to 350°–600°C. The bisulphate solution may then be returned to absorb fresh ammonia.[65]

Much attention has been given to the production of high-grade neutralised and powdered sulphate so as to obviate the destruction of packages and caking of the salt. C. G. Atwater and J. F. W. Schulze[66] attribute the caking property to the presence of pyridine sulphate, which attracts moisture. When such salt is neutralised by ammonia the sulphate is said to remain quite dry. J. T. Sheard[67] quotes experimental data from which it is concluded that neutral sulphate will absorb varying amounts of moisture according to the atmospheric conditions. It is not clear, however, how far atmospheric influences would penetrate into large masses of sulphate. In another case the caking is attributed entirely to the presence of free acid.[68] At all events it is generally considered that further alkali is needed to produce a non-caking salt, and this is effected in several ways. In some cases the process consists in adding dilute solutions of ammonia to the salt in the "whizzer," using the machine as a neutralising apparatus. It is advisable to draw off fumes of pyridine with a draught hood. A very ingenious method of obtaining this solution of ammonia is to condense the steam from the outlet of the finishing still (spent liquor outlet), which is said to give a solution of the required strength. The ammonia is thus recovered from waste.[69] Or the ammonia solution may be obtained by condensing part of the ammonia gases from the top of the finishing still on their way to the saturator. In an interesting paper E. V. Evans gives a detailed account of the process used at the South Metropolitan Gas Company's works, in which the ammonia solution is obtained in this way, and the neutralisation carried out in the whizzer at a temperature of 75° C. Afterwards the salt is dried in a current of hot air to a standard of 0·04% moisture.[70] In another case the crystals of sulphate and accompanying mother liquor are lifted out of the saturator by a mixture of ammonia gas and steam.[71] Or the salt may be simply sprayed with water at the moment of ejection from the saturator, a treatment which is supposed to break up the acid layer coating the crystals.

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[63] *Alkali Inspectors' Rept.*, 1919, 27.

[64] E.P. 137,345; *Gas J.*, 1920, **149**, 313; *J.*, 1920, 231A.

[65] Soc. Ind. de Prod. Chimiques, E.P. 136,833; *J.*, 1920, 516A.

[66] *Chem. and Met. Eng.*, 1920, **22**, 373; *J.*, 1920, 332A.

[67] *Gas World*, 1920, **72**, 542; *J.*, 1920, 515A.

[68] South Metropolitan Gas Co., E. V. Evans, and H. Hollings, E.P. 141,798; *J.*, 1920, 447A.

The chief trouble of such processes is the risk of increasing the amount of mother liquor beyond that which can be dealt with without introducing evaporating apparatus.

Other means consist of neutralising the whizzed salt with lime or other alkali, and at the same time drying it by passage through a rotating cylinder which is heated.[72] R. Lessing washes the sulphate of ammonia crystals with a saturated and slightly acid mother liquor at the same temperature so as to remove impurities which adhere to the surfaces. The mother liquor overflows and is filtered or settled before being returned to the saturator.[73]

Pyridine.

F. E. Dodge and F. H. Rhodes[74] propose to recover pyridine in a sulphate plant by allowing the saturator contents to collect pyridine until it begins to appear in the salt. The saturator contents are then discharged to a pyridine still and treated with gas rich in ammonia. The heat disengaged is sufficient to throw off the liberated pyridine which is condensed and salted out by solid sulphate of ammonia.

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[69] South Metropolitan Gas Co., P. Parrish, and W. A. M. Valon, E.P. 141,819 ; *J.*, 1920, 447A.

[70] *Gas J.*, 1920, **152**, 515.

[71] S. M. Shadbolt and J. E. Grainger, E.P. 144,030 ; *J.*, 1920, 544A.

[72] S. E. Linder and R. Lessing, E.P. 141,787 ; *J.*, 1920, 447A.

[73] E.P. 152,766 ; *Gas J.*, 1920, **152**, 461 ; *J.*, 1920, 819A.

[74] *Chem. and Met. Eng.*, 1920, **22**, 274 ; *J.*, 1920, 262A.

Concentrated Liquor.

The manufacture of concentrated ammonia liquor in gasworks has been largely discontinued and the plants converted to the manufacture of sulphate. "Household ammonia" is still made in some works, and there may be a demand in some cases for concentrated solutions for conversion to "nitre" gases by catalytic oxidation in acid-making works.

CYANOGEN.

Owing to the importance of cyanogen as a corrosive agent consideration has been given to the entire removal of cyanogen from the gas. For this purpose the Williams process is to be preferred owing to the efficiency obtained, which easily reaches 95%. In view of the product recovered it is not likely to offer such a good return as the ferrocyanide process, where the efficiency may be only 50%.

ETHYLENE.

The recovery of ethylene and its conversion into alcohol by E. Bury[75] has excited very general interest. An account of the process as adopted at Skinningrove is given in the Third Report of the Fuel Economy Committee of the British Association. After the removal of tar, ammonia, naphthalene, and benzol, it is proposed to remove hydrogen sulphide by the sulphur dioxide formed from the reduction of the sulphuric acid used in the absorption of the ethylene and concentration of the spent acid.[76] Propylene and higher olefines are removed by means of 80% sulphuric acid together with most of the water vapour. The gas is then heated at 60°–80° C. in a heat exchanger and scrubbed with 97% sulphuric acid heated to the same temperature. The time of contact is 2½ mins. and the efficiency 70%. The acid containing 5% of ethyl hydrogen sulphate is conveyed to a distilling column and diluted with steam. The temperature of the reaction is sufficient to drive off the alcohol from the hydrolysed sulphate. The dilute acid is then concentrated for further use.

F. S. Sinnatt and L. Slater[77] have examined the hydrocarbons in coal gas by passing such gas, containing 3·5–4·0% of hydrocarbon soluble in fuming sulphuric acid, through bromine water for 10—21 days. The brominated compounds were then removed and examined. On distillation under reduced pressure (15 mm.) and fractionation the dibromides of ethylene, propylene, butylene, and amylene were obtained. The weight of these indicated that the hydrocarbons in the gas were present in the proportion by volume of ethylene 84·8, propylene 11·8, butylene 2·3, amylene 1·5.

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[75] E.P. 147,360; *J.*, 1920, 94A, 593A.

[76] *See* Debus, *J. Chem. Soc.*, 1888, **53**, 278.

[77] *Analyst*, 1920, **45**, 85; *J.*, 1920, 288A.

Some interesting work is described by J. A. Smythe[78] in which ethylene is chlorinated directly, using calcium chloride as catalyst. Dichloroethane and trichloroethane are the chief products, and by fractionation they may be obtained practically pure. The reaction generates sufficient heat to necessitate cooling arrangements. Coal gas treated at the rate of 3 cb. ft. per hr. with chlorine in presence of calcium chloride yielded 120 grams of oil which contained a large number of chlorinated products of the unsaturated hydrocarbons, including those mentioned. This oil also contained relatively large amounts of benzene and toluene in solution.

The separation of ethylene, benzene, and acetylene quantitatively is effected by W. B. Treadwell and F. A. Tauber[79] by absorbing acetylene in a solution of mercuric cyanide in sodium hydroxide and ethylene in a solution of mercuric nitrate dissolved in a saturated solution of sodium nitrate and dilute nitric acid. Propylene behaves like ethylene, but benzene is unaffected by either reagent.

NAPHTHALENE.

A great deal of attention is still given to naphthalene. Although it was supposed that oil-washing for benzol recovery during the war would accentuate the trouble and that carburetting was essential, it is now found that the closing down of both oil-washers and carburettors brings back all the old troubles in a worse form. It is difficult to place the responsibility of such troubles, as the atmospheric conditions varying with the seasons play such an important part. There is little doubt, however, that the reduction in the naphthalene content of the gas which can be effected with oil-washing followed by some form of carburetting gives great relief. Vaporising paraffin or atomising it and spraying it into the gas stream is being widely adopted. The practice of coke ovens is very effective. In this the bulk of the naphthalene is removed by suddenly chilling the hot gas by means of cold water sprays in scrubbers, when the naphthalene is easily separated in the form of sludge. Subsequent washing of the gas by oil leaves hardly one grain per 100 cb. ft.

C. Ab-der-Halden[80] has given the results of an extended research on the so-called "carrying power" of vapours. Coal gas saturated with naphthalene to which portions of various petrol and tar oils were subsequently added was passed through a capillary tube immersed in a cooler at known temperatures. The point at which the naphthalene was deposited was marked by the extinction of the flame of the issuing gas. It was found that when a carburetting oil was added naphthalene might exist in the gas in amount above that when no carburant was present without deposition. This supersaturation did not depend on the chemical constitution of the carburant but on its volatility. Those fractions of petrol and tar-oil boiling between 80° and 90° C. exert the most influence. Thus for toluene an addition of under 10 g. per cb.m. produced a maximum lowering of the point of deposition of 1° C.; for xylene this was practically nil, but for benzene over 1° C.; 20 g. of the latter per cb.m. gave a reduction of nearly 2° C. Unfortunately, on lowering the temperature from 25° C. to 15° C. the carrying power of the carburant was very much less marked. In considering these results it ought to be remembered that the introduction of a petrol or tar oil affects the vapour pressure of the naphthalene and the amount capable of existing as vapour at a particular temperature is reduced. To this the "carrying power" of a carburant may be due.

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[78] *Gas J.*, 1920, **149**, 691; *J.*, 1920, 312A.

[79] *Helv. Chim. Acta*, 1919, **2**, 601; *J.*, 1920, 4A.

[80] *Chim. et Ind.*, 1920, **3**, 19T; *J.*, 1920, 219A.

TAR AND TAR PRODUCTS.

Recent years have seen the introduction of continuous tar distillation plant with a considerable amount of success. Such plant is particularly suitable for gaseous firing and is not nearly so successful with solid fuel direct-firing. The latter method does not provide the continuity of conditions essential for steady, continuous working. Units of continuous plant are not yet of the requisite capacity to keep working costs down if one or more furnaces need attention on each plant. The chief trouble—and this applies to all tar distillation—lies in the preliminary dehydration of the tar, which is usually effected in heat-exchangers. Trouble in this direction leads to irregularity in the feed to the stills. Fractionation is not usually so good in continuous plant, but there seems to be no reason why means should not be employed for effecting better division of the products. W. E. Edwards,[81] for example, patents a continuous plant with only two stills, in the last of which the creosote and anthracene fractions are removed together and separated by fractional condensation.

Trouble with chloride in tar distillation is more frequent when dealing with coke-oven tar, or gasworks tar from retort houses using dry mains. It has been satisfactorily avoided by washing the tar in old boilers with exhaust steam. The temperature and capacity of the boilers is such that a good settling out of liquor occurs, the water content of the tar being reduced to less than 3% before entering the heat-exchangers.

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[81] E.P. 139,263; *J.*, 1920, 328A.

R. Hodurek[82] finds that the free carbon in tar as separated in the usual manner contains bituminous substances which are precipitated from tar by alcohol, benzol, petroleum, ether, acetone, etc., but are soluble in anthracene oil. Possibly these are some of the pitch oils of Ab-der-Halden.[83]

R. M. Chapin[84] describes a method of estimating phenol in presence of other phenols based on the red coloration produced by Millon's reagent. The method is said to be sensitive to a minimum of 0·04 mg. of phenol in presence of 4 mg. of cresol in a volume of 4 c.c. F. Fischer and P. K. Breuer[85] use the Müller method of fractional precipitation with hydrochloric acid.

An excellent description of the manufacture of pure naphthalene is given by J. A. Davy.[86] The crude salt is distilled and pressed in a steam-heated hydraulic press, which removes all but 1% of the 25–30% of oil. It is then acid-washed, again distilled, broken up, and ground. The finished salt melts at 79·5°–79·7° C. The yield is 40–45% of the crude salt. According to R. Kutschenreuter[87] naphthalene is recrystallised from hydronaphthalenes and in this way obtained very pure. By hydrogenation naphthalene may be made available for motor spirit.[88] Thionaphthene has been isolated by a series of step sulphonations of crude naphthalene[89] and diphenylene sulphide in crude phenanthrene.[90]

The separation and purification of carbazole has excited much attention.[91] In one process crude carbazole is obtained from the crude pyridine used in washing anthracene or the potash lye produced by heating anthracene with caustic potash, and is recrystallised twice from phenol or other tar acids, giving a 90% product.

Low-temperature Tars.

The extensive investigations of F. Fischer and colleagues[92] are continued. On distillation 14–30% of the tar was obtained up to 225° C., containing phenolic substances which attacked metal. From 225° to 300° C., 25–30% of oil was obtained with a flash-point of 60°–65° C., calorific value 8620 cals., viscosity at 20° C.–5° Engler. From 300°–325° C. there was 15–20%, from which solid paraffin separated to the extent of 0·5% of the weight of tar, and there was also present much heavy phenol. The pitch contained less free carbon than ordinary pitch. Up to 50% of the tar was soluble in alkali, and although carbolic acid was not found or was present only in very small quantity, all three cresols were isolated together with xylenols, trimethylphenols, etc. A large-scale distillation yielded 1·5% of catechol with a 50% extraction. The possibility of producing lubricating oils is interesting, but owing to the instability of the phenols present under heat treatment they would probably have to be removed.

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[82] *Mitt. Inst. Kohlenvergasung*, 1919, **1**, 9, 19, 28; *J.*, 1920, 622A.

[83] *Gas J.*, 1913, **123**, 46.

[84] *J. Ind. Eng. Chem.*, 1920, **12**, 771; *J.*, 1920, 652A.

[85] *Chem. Zentr.*, 1919, **90**, IV., 1032; *J.*, 1920, 261A.

[86] *Gas J.*, 1919, **148**, 489; *J.*, 1920, 8A.

[87] G.P. 317,634; *J.*, 1920, 398A.

[88] G.P. 300,052; *J.*, 1920, 743A.

[89] R. Weissgerber and O. Kruber, *Ber.*, 1920, **53**, 1551; *J.*, 1920, 716A. *See also J.*, 1920, 777A.

[90] *Ber.*, 1920, **53**, 1566; *J.*, 1920, 717A.

[91] *Cf.* E.P. 139,441; *J.*, 1920, 291A. E.P. 139,981; *J.*, 1920, 328A. E.P. 121,455; *J.*, 1920, 59A.

[92] *See J.*, 1920, 150A, 151A, 223A, 261A.

Evidently we are only on the fringe of the possibilities opened up by the properties of low-temperature tar and the commercial success of the process may well depend on the results of further work on this line.

Benzene. Toluene.

A certain number of benzol recovery plants washing coal gas for town use have remained in operation and others have been re-started. Reduction of town supply to a thermal basis, the tendency to restrict inerts, and the increasing demand for home-produced spirit have placed the process on a sound basis. The commercial prospects depend largely on the value attributed to the hydrocarbons removed from the gas. This may be equitably worked out as follows :—To the cost of each gallon of crude benzol recovered is added the cost of manufacture, including capital charge and maintenance of plant, of an amount of gas sufficient to make up for the thermal units removed from the gas. There is also a charge to cover extra cost of distributing a larger volume of gas per therm. Assuming a recovery of 2½ gallons of crude benzol per ton of coal carbonised containing 18 lb. of products derived from the gas of calorific value 16,500 B.Th.U. per lb., and allowing a loss of 5% in recovery, there has been removed from the gas a total of 311,800 B.Th.U. or, say, 1¼ therms per gallon of crude benzol. With a cost price of 4d. per therm and adding 1d. for the additional cost of distributing a 5% lower grade gas, there is a total of 6d. to be added to the cost of the recovery of each gallon of crude benzol.[93]

In the recovery of crude benzol with wash-oil containing much naphthalene the latter has been removed by taking off the heavy oil from the bottom of the column of the crude still and distilling it with closed steam ; after returning the volatile products to the main crude benzol condenser the residue is allowed to cool and the naphthalene separated.[94] This practice is not necessary where the plant includes refining stills, as the naphthalene is then separated from the still-bottoms.

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[93] F. Nicholls, Newcastle Chemical Industry Club, Dec. 7th, 1920.

Grébel[95] gives an interesting account of the Brégeat process in which cresols are used for absorbing benzol from coal gas. The mixture of cresols used is very fluid even at -18° C., boils at 185°-203° C., and is only slightly soluble in water. The absorbing power is over three times as great as that of creosote oil, and hence the bulk of liquid to be debenzolised is very much smaller.

Paraffin oil has also been used as wash-oil and provides a very clean medium.

E. H. Bird[96] describes a double coil scrubber for use in estimating hydrocarbons by absorption from gases which saves a cumbrous train of wash-bottles.

The interesting process of H. G. Colman[97] for removing carbon bisulphide from benzol fore-runnings so as to render them available for motor spirit, is to be tried commercially and should be successful. The carbon bisulphide is removed by washing with an alkali disulphide, when the perthiocarbonate formed can be removed in solution. Another patent[98] aims at preventing sulphonation of benzene in the ordinary process of acid washing by using a weaker acid at a higher temperature. The hot vapours or liquid are passed into a sulphonator kept at the required temperature so that thiophene may be sulphonated without the benzol being appreciably attacked.

In the treatment of acid tar the latter may be placed in shallow retorts and steamed.[99] The vapour, which contains acid constituents as well as hydrocarbons, is treated with ammonia gas or liquid and the excess of ammonia removed by washing with weak acid. The vapours are then condensed.

A good deal of work has been done both at home and abroad on the catalytic oxidation of benzene and its homologues. Such reactions offer considerable possibilities. H. D. Gibbs[100] claims an 82% conversion of naphthalene by oxidation in the presence of vanadium oxide. J. M. Weiss and C. R. Downs[101] now give the results of research on the oxidation of benzene to maleic acid, toluene to benzaldehyde and benzoic acid, naphthalene to phthalic acid, and anthracene to naphthaquinone. Benzene can also be oxidised to quinone at the anode of an electrolytic cell and afterwards reduced to quinol.[102]

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[94] *Gas J.*, 1920, **152**, 83.

[95] *Le Génie Civil*, Nov. 8th, 1919 ; *Gas J.*, 1920, **149**, 364, 432.

[96] *Chem. and Met. Eng.*, 1920, **22**, 705. *Cf.* U.S.P. 1,316,602 ; *J.*, 1920, 283A.

[97] E.P. 145,099 ; *J.*, 1920, 567A.

[98] E.P. 152,470 ; *Gas World*, 1920, **73**, 385 ; *J.*, 1920, 777A.

[99] E.P. 152,054 ; *Gas J.*, 1920, **152**, 460 ; *J.*, 1920, 777A.

[100] *J. Ind. Eng. Chem.*, 1919, **11**, 1031 ; *J.*, 1920, 100A.

[101] *J. Ind. Eng. Chem.*, 1920, **12**, 228 ; *J.*, 1920, 397A ; also *J.*, 1920, 9A, 44A.

Motor spirit is obtained by passing heavy tar oil vapours over red-hot coke in the presence of steam, when hydrogenated products result.[103] The production of lubricating oils is claimed by heating creosote and tar oils under pressure or with a reflux condenser at 400° C. in presence of a catalyst.[104]

Useful information is given by H. Moore[105] on the temperature of spontaneous ignition of mixtures of benzol and petrol. The temperature taken is that at which a substance surrounded by air or oxygen at the same temperature will burst into flame without the application of a spark or other local high temperature. The following table shows the ignition points of mixtures of benzol and petrol :—

Benzol. %	Petrol. %	Ignition point.
100	0	630° C.
90	10	481
80	20	303
70	30	290
10	90	283
0	100	272

WATER GAS.

H. L. Nicholson[106] gives some interesting experiences gained by varying the amount of steam used on the "down" runs and "up" runs in the generation of water gas. By increasing the proportion of steam used on the down run and keeping all the blast on the up run the results were improved. Theoretically this could be carried to the extreme so that the steam on making its way down would meet an increasing temperature, but in practice some steam is needed on the up run to keep the grates and metal work of the generator from becoming overheated. E. G. Stewart[107] regards this procedure as of limited use owing to the risk of extinguishing the top portion of the fire. He also finds that the tendency of carbon dioxide in the blast products to reduce to carbon monoxide limits the temperature normally to about 1800° F. A high carbon dioxide content of the blast gases can be secured by reducing the time contact, for example, by using a shallow fuel bed coupled with a high blast velocity. It is, however, very easy to get a gas very rich in carbon monoxide with a thin but even fuel bed. Stewart gives the losses by radiation and convection from the apparatus as being 5–15% of the total heat energy of the fuel, and the overall efficiency of the process up to 58%. The adaptation of the waste heat boiler for recovering heat from both the "blast" and "make" gases should be a real economy. An installation described fitted to a unit of 1½ million cb. ft. capacity is said to bring the thermal efficiency of gasification to about 70%. The boiler evaporates 8000 lb. of water per fuel hour at 100 lb. pressure and supplies all the steam required for the plant.

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[102] U.S.P. 1,322,580 ; *J.*, 1920, 100A.

[103] G. F. Forwood and J. G. Taplay, E.P. 145,198 ; *Gas J.*, 1920, **151**, 345 ; *J.*, 1920, 651A.

[104] G.P. 310,774 ; *J.*, 1920, 327A, 441A.

[105] *Gas J.*, 1920, **149**, 245. *See also J.*, 1920, 217A.

[106] *Gas J.*, 1920, **150**, 85.

[107] *loc. cit.*

TOWN GAS.

The cheap and economical supply of heat units in a gaseous form is not the only condition the gas industry has to fulfil. The supply of heat units must be given at a sufficient rate and in a sufficiently concentrated condition to suit the requirements to which the gas is to be put. These uses are increasing daily, and are very diverse. What is quite suitable and possibly cheaper for one purpose may not be for another. A great deal will naturally depend on local conditions. Considerable progress has been made during recent years in providing information on which a reliable policy may be based, but it must be admitted that very little care was formerly exercised in correlating the quality of the gas, the purpose for which it was to be used, and the apparatus. The superior results obtained from existing apparatus with low grades of gas show that considerable loss of efficiency must have occurred in pre-war days, and that in many cases the consumer has obtained benefit from a reduction in quality. Owing to the importance of such factors as the size and shape of flame no apparatus can be adjusted to suit all the varying qualities of the gas manufactured to-day and still give a maximum efficiency with all. Another factor which is often lost sight of is the improvement effected when the mixing of air and gas is intimate. On this account low-grade gas is easier to manipulate, and probably to this is partly due the claim of low-grade gas to be considered as superior in itself to high-grade gas.

In some very interesting work, C. Killing[108] has investigated the Bunsen flame by the use of platinum and platinum-iridium wires of various thicknesses. He finds that at the tips of the small inner green cones of a Meker flame the temperature is considerably higher than inside the main mass of flame. With inverted burners the temperature is similarly distributed but somewhat lower owing to the radiation and conduction losses from the burner nozzle. In this case the small green cones become longer and readjustment of the air supply is necessary. By substituting a refractory gauze of less conductivity the temperature of the tips of the cones is found to be higher. The results are applied to a burner in which the green cones are suitably developed and a mantle brought close to their tips.

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[108] *Gas World.* 1920, 72 586 *J.*, 1920, 540A

An ingenious inverted burner is described in which gas and primary air are introduced inside the mantle by a narrow passage between a centre pipe and the mantle support. The products of combustion leave by the centre pipe, so inducing a draught which pulls the secondary air through an aperture in the almost enclosed globe and through the mantle.[109]

H. Davies, in the course of work on the production of silent flames,[110] concludes that noise is not necessarily due to imperfect mixing of gas and air or to eddies. A flame was noisy if a critical consumption was exceeded depending on the length and bore of the tube. This consumption was a maximum for a particular composition of gas-air mixture. It is suggested that the production of a silent flame depends on a condition of differential velocity in the stream of gas-air mixture issuing from the flame orifice.

Several further papers have been published on the propagation of flame velocity.[111] The mixture CH_4+2O_2 has the fastest speed of uniform movement of flame of any mixture of oxygen and methane, and addition of oxygen, methane, or nitrogen to this mixture results in diminution of the speed. Methane has the greatest effect in retarding the speed, nitrogen next, and oxygen least. The speed of detonation is increased by addition of methane. Increase of oxygen diminishes both.

High velocity of combustion is obviously desirable for high-temperature work. H. Strache considers that in mixtures of water-gas and coal-gas the former compensates for lower calorific value by the increasing velocity of combustion and higher flame temperature. It is interesting to note that W. H. Battersby finds that atmospheric conditions influence the behaviour of gas in burning, and that during winter months, to give satisfactory results in respect to the danger of back-firing, the calorific value should be 15 B.Th.U. higher than in summer.[112]

The first part of the Third Report of the Joint Research Sub-Committee of the Institute of Gas Engineers and University of Leeds[113] deals with low-pressure upright incandescence burners and the effects of inerts on lighting. The effect of each inert is studied separately, so that the percentage composition of the combustible gas was unaltered. With higher grade gas delivering over 2500 B.Th.U. per hr. net to the burner there was a falling off in efficiency owing to incomplete aeration, the burner then being unsuitable. Up to a limit of 26·5% nitrogen the introduction of this gas as a diluent had practically no effect on the efficiency value of lighting. With upwards of 30% of nitrogen somewhat lower efficiencies and lighting values were obtained. It was found that the mere opening of the nipple orifices is not universally applicable as a means of supplying the increased flow of gas necessary for a low grade gas to supply the number of B.Th.U. per hr. required, as proper aeration may not be effected. With carbon dioxide as inert the results were very much inferior, and while with 8% of carbon dioxide a good efficiency and lighting value were obtained, better results were given when 8% of nitrogen replaced the carbon dioxide. With air as inert the results were similar to those given when the full amount of air was admitted at the burner, as is usual. Trouble was experienced owing to the varying specific gravity of the gas, and it is suggested that for permanent use such a mixture would require a special burner. It is considered incorrect for some purposes to include air (nitrogen accompanied by the atmospheric proportion of oxygen) as inert. W. B. Davidson[114] contributes to the subject, and refers particularly to the use of gas for high-temperature work where the difference between high- and low-grade gas may mean the difference between success and failure. He refers to a previous paper,[115] wherein it was shown that with 10% of carbon dioxide coal-gas flame showed a reduction of temperature of 55° C. measured in the centre of a Méker burner, while with 10% of nitrogen the reduction was 45° C. Similarly with incandescence lighting there was a reduction of 17·7% for 10% of carbon dioxide and 12·5% for a similar percentage of nitrogen. The first addition of nitrogen made an appreciable reduction in the candle-power per thermal unit.

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[109] E.P. 146,656 ; *Gas J.*, **151**, 347.

[110] *Gas J.*, 1920, **152**, 395 ; *J.*, 1920, 812A.

[111] W. Payman, *Chem. Soc. Trans.*, 1919, **115**, 1436, 1446, 1454 ; *J.*, 1920, 94A, 95A. *Chem. Soc. Trans.*, 1920, **117**, 48 ; *J.*, 1920, 181A. W. Mason and R. V. Wheeler, *Chem. Soc. Trans.*, 1920, **117**, 36 ; *J.*, 1920, 181A. *Chem. Soc. Trans.*, 1920, **117**, 1227 ; *J.*, 1920, 775A.

[112] *Gas J.*, 1920, **151**, 393.

[113] *Gas J.*, 1920, **150**, 392 ; *J.*, 1920, 508A.

In the second part of their Report[116] the Sub-Committee deal with the influence of inerts on gas fires. The radiant efficiency was taken as index to variations in thermal efficiency. The maximum efficiency was obtained when about 13,000 B.Th.U. per hr. were supplied. It is pointed out that when a fire is subjected to an overload the efficiency may be interfered with. With a 20% overload the lower grades of gas suffer less than the higher grades; this is one reason why the lower grades of gas appear in themselves more efficient than the higher grades. If the flames were fairly well aerated and the tips just short of coming through the heads of the radiants, the gas rate corresponding to the maximum efficiency was closely approached but usually 10% too high. With air as diluent to a rich gas the results were improved owing to better aeration but otherwise the addition produced no difference. Nitrogen may be added up to 20% without deleterious effect, and even when used to bring the calorific value down to 300 B.Th.U. gross the effect is not great. Carbon dioxide has a much greater effect in reducing the efficiency but not to an important extent unless over 5%. Blue water-gas and mixtures of this with coal gas increase the radiant efficiency. The conclusion is come to that in any mixture likely to be proposed for public supply the effects of inerts may be disregarded as far as gas fires are concerned.

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[114] *Gas J.*, 1920, **151**, 23, 78.

[115] *Gas J.*, 1913, **122**, 948.

[116] *loc. cit.*

The viscosity of complex gas mixtures cannot be accurately calculated from the proportions of their components, but may be measured in an apparatus described by M. Höfsass[117] in which the viscosity is compared to that of air by the rate of flow through a fine capillary. Various curves for coal gas of differing compositions are shown. The following table gives data for some gases.

	Coal gas.	CO, N_2.	CO_2.	C_2H_4.	CH_4.
Relative density	0·595	0·967	1·52	0·967	2·694
Viscosity	0·738	0·968	0·840	0·574	0·417
Relative viscosity modulus	1·240	1·00	0·553	0·593	0·155

The subject of corrosion is always interesting and important and the investigation of the "Life of Gas Meters" Sub-Committee of the Institute of Gas Engineers[118] gives a clear view of the manner in which internal corrosion is carried on. The main corrosive action is attributed to (1) a combination of cyanogen, ammonia, and water; (2) carbon bisulphide, ammonia, and water; (3) carbon dioxide, oxygen, and water; (4) sulphur dioxide and water. It is considered that sulphur dioxide may find its way into town gas from the addition of "blue gas," but this gas and ammonia should be removed in the course of ordinary purification. Whether, even provided that these gases were never allowed to pass, it would also be worth while to remove the whole of the cyanogen, oxygen, and carbon bisulphide in order to reduce corrosion is somewhat doubtful. The suggestion of the Committee simply to remove sufficient water from the gas to prevent its deposition in a liquid form at any subsequent time is much more feasible, though naphthalene would probably also have to be removed. The method proposed consists of compression, cooling, separation of condensed water, and then expansion into the mains.

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[117] *J. Gasbeleucht.*, 1919, **62**, 776; *J.*, 1920, 219A.

[118] *Gas J.*, 1920, **150**, 583; *J.*, 1920, 508A; see also A. R. Myhill, *Gas World*, 1920, **72**, 265.

The Gas Regulation Act.

It must be admitted that the Gas Regulation Act is framed wisely to ensure constancy in supply both in quality and pressure rather than with a view to provide some particularly grade of gas.[119] The Act places the onus of regulation on the Board of Trade subject to the Orders given, including provision that the gas must be free from hydrogen sulphide and shall have a minimum pressure of 2 in. water pressure on a 2-in. diam. pipe. The Board of Trade is to hold an enquiry into the desirability of placing a limitation on the amount of carbon monoxide and inert gases present. Among the conditions of testing gas to be imposed is a provision for the use of a recording calorimeter in the case of those concerns supplying over 100 million cb.ft. per annum, a clause which should go far to preserve uniformity in the supply. For a deficiency in calorific value for 2 hours or upwards on any one day of more than 5% below the declared calorific value a penalty of £5 is imposed for every 1% over the 5%. The penalty for lack of purity or pressure is not to exceed £10. Further penalties are to be imposed if the average calorific value for any quarter is less than the declared value. The particular concern may declare any calorific value they may think fit to supply and Special Orders may be given for the supply of industrial gas, as distinct from the common town supply, and also for obtaining gas in bulk from outside sources. Under the Act standard charges may be revised and placed on a "therm" basis. (One therm = 100,000 B.Th.U.) The Board of Trade are to appoint three Gas Referees and a Chief Gas Examiner, and are to prescribe conditions of testing—in particular of suitable types of recording calorimeters. The latter may be a matter of some difficulty. The experience of the writer, extending over many years, of several different types is that an accuracy of +1% can be maintained provided that the instruments are attended to regularly every day by competent persons and provided that they are set up in clean and suitable positions. Without these provisions trouble and annoyance will be endless.

The Fuel Economy Committee of the British Association are not satisfied with the conditions imposed by the Act, but according to a deputation to the Board of Trade hold that the basis should be a nett calorific value, the minimum gas pressure should be altered, cyanogen should be eliminated on account of its poisonous character, and for the same reason, and also on account of its high "kick" on explosion, carbon monoxide should be restricted to 20%. Owing to the slow rate of flame propagation of methane and its smaller range of explosion, this gas should be present to an extent of not less than 20%. Finally the minimum calorific value supplied should be 450 B.T.U. gross.[120]

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[119] *Gas J.*, 1920, **151**, 292; **150**, 425.

[120] *Gas J.*, 1920, **149**, 320.

L. Vignon[121] also advocates the removal of carbon monoxide and suggests alternative methods. In one the carbon monoxide is converted into methane by passage over finely-divided nickel at 250° C., first removing benzene and sulphur compounds. Secondly, it may be converted into carbon dioxide by reaction with iron oxide at 900° C., previously removing benzene and subsequently the carbon dioxide formed. A third alternative consists in the absorption of the gas in ammoniacal cuprous chloride.

In respect to the danger of carbon monoxide the work of A. Kling and D. Florentin[122] is particularly interesting. It is found that carbon monoxide may be present in the products of combustion if there is any sudden cooling of the flame. The amount coming into the air by leakage from piping and fittings of an interior supply of 15 taps, the gas containing 20% of carbon monoxide, is much less than that produced in the same time by burning the same gas in a small furnace or Auer incandescent burner.

There is a limit to the number of restrictions which it is advisable to impose on an industry. A charge on the thermal units and the natural competition of electricity should be sufficient to safeguard the public against the supply of gas which is in any way dangerous.

The old form of sliding scale, while fair enough when first imposed, did not offer any great incentive to progress in the gas industry. The increasing cost of materials and labour has more than counterbalanced improved methods of working so that the latter have not received their just reward. Hence it is interesting to find a scheme of sharing surplus profits between the consumers, the shareholders, and the employees, included in the Parliamentary Bill of the South Metropolitan Gas Company. There is also an arrangement for obtaining benefit for special reduction of the sulphur compounds to a point when not more than one volume of carbon bisulphide vapour is present in 40,000 volumes of gas.[123]

[121] *Ann. Chim.*, 1920, **13**, 284; *J.*, 1920, 591A.
[122] *Comptes rend.*, 1919, **169**, 1404; *J.*, 1920, 147A.
[123] *Gas J.*, 1920, **151**, 340.

MINERAL OILS.

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Whilst there are no features of outstanding interest on which to report, the year under review has afforded evidence of steady progress in all departments of petroleum technology and welcome signs that active research is being prosecuted not only on problems of actual immediate importance such as cracking—or pyrolysis—but on the more general lines forecasted in last year's report. In this connexion a very complete and valuable paper contributed by W. A. Hamor[1] deserves serious consideration.

The Problems of the Petroleum Industry.

Hamor states that at the close of 1919 approximately 4,986,300,000 brls. of crude oil had been produced in the United States since the first well was drilled in 1859. This is about 43 % of the original recoverable content, as estimated by the U.S. Geological Survey. According to conservative estimates the recoverable crude petroleum in America would probably be practically exhausted in seventeen years if the 1919 rate (nearly 380,000,000 brls.) of production were maintained. Hence production of petroleum in the United States must pass its peak at an early date—probably within five years and possibly within three years. Experts believe that the most conspicuous developments affecting the source of the world's supply of petroleum in the next decade will occur in the countries that border the Caribbean Sea and the Gulf of Mexico. Within the last four years the annual production of petroleum in Mexico has increased from 21,000,000 brls. to 56,000,000 brls. and the potentialities of future production in that country have been demonstrated.

Production can only be maintained by: (1) Obtaining greater supplies of crude oil (*a*) by increasing importations ; (*b*) by developing a shale oil industry ; (*c*) through increased recovery from oil fields and elimination of wastes in production. (2) A better utilisation of the crude now available, principally (*a*) by the pyrolysis of fuel oils into gasoline ; (*b*) by developing gasoline substitutes; (*c*) through the development and use of Diesel-type engines utilising the heavier fuel oils.

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[1] *Chem. and Met. Eng.*, 1920, **23**, 425.

Among the development and production problems mentioned by Hamor are the dehydration of emulsified petroleum and the prevention of its formation in oil wells, and the determination of the capacities and characteristics of oil and gas sands. Among the subjects cited as requiring investigation in refinery technology are the conversion of distillation products of residue or heavy oils into saturated hydrocarbons, *e.g.*, by hydrogenation; the polymerisation of olefines; the influence of temperature on the acid treatment of distillates; the treatment of lubricating oils to minimise losses by emulsification; the isolation of pure naphthenic acids of high molecular weight from waste lyes; and the utilisation of the esters from the naphthenic acids contained in the residue from the alkali treatment of oils.

Petroleum Hydrocarbons as a Basis for Synthetic Chemistry.

The occurrence of so many diverse hydrocarbons in mineral oil leads to the expectation that a synthetic chemistry such as originated from the benzene series must ultimately be developed. Petroleums probably contain all of the normal paraffin hydrocarbons up to $C_{26}H_{54}$, and perhaps further in the series, and also most of the more stable naphthenes which are theoretically possible but for the most part yet unknown.[2]

It is to be anticipated that petroleum will constitute the basis of a chemical products industry which will be as distinct in scope and activity as the coal-tar industry of the present time, and amongst some of the initial achievements may be indicated the claim by the De Bataafsche Petroleum Maatschappij that an oil, the drying properties of which are comparable with those of linseed oil, may be obtained by chlorinating a mineral oil fraction of sp. gr. 0·885 with the subsequent removal of hydrogen chloride; and the production of artificial resins by the chlorination of petroleum and its distillates. Thus the obvious line of attack *via* chlorination and subsequent treatment of the halogen derivatives has already been exploited to a limited extent.

The synthesis of glycols from the olefines present in oil gas affords another avenue for attack.[3] The simpler glycols have frequently been proposed as substitutes for glycerin, but until quite recently a satisfactory method for their commercial manufacture has been lacking. B. T. Brooks and I. W. Humphrey[3] have shown that the conversion of ethylene chloride to glycol proceeds readily when the former is heated under pressure with methyl alcohol and an alkali formate, ethylene diformate being formed as an intermediate product; the conversion of ethylene and propylene chlorohydrins into the corresponding glycols may be effected by heating with aqueous bicarbonate or carbonate solutions.

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[2] B. T. Brooks, *Chem. and Met. Eng.*, 1920, **22**, 933.

[3] B. T. Brooks, *Chem. and Met. Eng.*, 1920, **22**, 629; *J.*, 1920, 384A.

Oil-gas containing 35–45% of olefines, still gases from petroleum cracking stills, containing 10–12% of olefines, and ethylene made by the decomposition of alcohol are the only sources of ethylene and propylene of practical importance, but ethane and propane are partially converted into ethylene and propylene by heat and the monochlorides are almost quantitatively decomposed to the corresponding olefines by passing the vaporised chlorides over pumice impregnated with barium chloride and heated to 200°–250° C.

K. P. McElroy[4] has patented a novel and ingenious method of manufacturing chlorohydrins from ethylene or oil-gas which consists in passing the olefines into a mixture of steam and chlorine, whilst very excellent yields of ethylene chlorohydrin may be obtained by passing chlorine and ethylene into cold water, with vigorous agitation to promote the solution of the two gases.

The lowest boiling fractions of petroleum, of the composition C_5H_{12}, may be used for the preparation of isoprene. By systematic chlorination, isomerisation, and liberation and addition of hydrochloric acid, the three hydrocarbons present (iso- and normal pentane and tetramethylmethane) all can be converted into isoprene.

If a simple, direct process for obtaining the butadiene hydrocarbons from petroleum can be found, a good route to synthetic rubber will be opened up. E. Pyhälä has shown that the fraction of Baku petroleum boiling between 98° and 106° C. yields up to about 20% of its weight of adipic acid, which, by the way of the amide, can be converted into butadiene.

It may be noted that the production of dyestuffs from petroleum is an open field. Kharitchkov has found that the nitro-derivatives obtained by treating machine or spindle oils with warm nitric acid are related to the nitro-compounds obtained by nitrating polynaphthenic acids and used in the preparation of dyestuffs. Nitro-products which yield with alkalis brown substantive dyestuffs and with sulphur brown to brown-violet sulphur dyestuffs, have been obtained by the nitration of the higher fractions from Galician petroleum. The preparation of aromatic hydrocarbons from aliphatic hydrocarbons—especially the preparation of benzene and its homologues from petroleum—requires somewhat more investigation; incidentally crude petroleum from some Eastern fields are aromatic-rich and provided toluene for explosive manufacture during the European war.

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[4] U.S.P. 1,253,616, 1,295,339; *J.*, 1918, 167A; 1919, 339A.

In this connexion the Skinningrove experiments are very much to the point, and it appears that an alternative method of utilising the olefines produced in cracking is here indicated.[5] Durham coking coal gives a gas containing 2·0–2·4% olefines consisting chiefly of ethylene. This is absorbed by means of 95% sulphuric acid, and the ethyl hydrogen sulphate thus formed is subsequently hydrolysed by dilution of the acid with water, yielding alcohol and sulphuric acid. It was found that at temperatures between 60° and 80° C, the time of contact between gas and acid required for a 70% absorption of the ethylene was only 2¼ minutes, and that under these conditions ethyl hydrogen sulphate was the only product formed. At lower temperatures decomposition occurs. Prior to the ethylene absorption, tar, ammonia, naphthalene, benzol, hydrogen sulphide, higher olefines, and water vapour are removed from the gas in the order named. The propylene and other higher olefines, together with 97% of the water vapour, are removed from the gas by means of 80% sulphuric acid at ordinary temperatures. The removal of the ethylene is carried out on the counter-current principle, the acid being used until it has absorbed 5% by weight of ethylene. The acid is then taken to a distilling column, where it meets a current of steam, which reduces its strength to 75% and hydrolyses the ethyl hydrogen sulphate, the heat of dilution being sufficient to effect the distillation of the alcohol, which leaves the plant at 95% strength. The diluted acid is re-concentrated in a Gaillard tower and is then ready for further absorption of ethylene.

CHEMISTRY OF PETROLEUM.

F. J. Skowronski[6] has shown that petroleum from Tustanowic after fractionation and purification contains hexanaphthene (cyclohexane), heptanaphthene (methylcyclohexane), octanaphthenes (1.2-, 1.3-, and 1.4-dimethylcyclohexanes), mononaphthene (1.2.4-trimethylcyclohexane), *a*- and *β*-decanaphthenes, and also hexahydro-*p*-xylene (not hitherto observed in petroleum). The decanaphthenes appear to be dimethylethylcyclohexanes. Galician oil is thus shown to be intermediate between American and Russian oil in its naphthene content.

J. Tausz[7] has pointed out that although the three xylenes and ethylbenzene have been found in coal tar only *m*- and *p*-xylene have been previously isolated from crude petroleum. C. F. Mabery[8] sought for *o*-xylene and ethylbenzene in petroleum, but unsuccessfully. Tausz has been able to prove that such a difference does not exist, and quotes the percentage of ethylbenzene and the xylenes found in seven samples of crude petroleum from different localities.

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[5] *J.*, 1920, 308R, 94A.

[6] *Metan*, 1918, 61 *et seq.*; *J.*, 1920, 438A.

[7] *Z. angew. Chem.*, 1019, **32**, 361.

[8] *Proc. Amer. Acad.*, 1895, **21**, 60.

W. Steinkopf and F. Beiersdorf[9] found that no inversion of the sign of rotation was produced by the catalytic hydrogenation of Java petroleum fractions, and the very slight alterations observed in the magnitude of the specific rotation appear to indicate that optical activity is caused by the presence of a saturated compound which is not affected by hydrogenation. The rotation cannot be due to the presence of cholesterylene, since this, when catalytically hydrogenated, yields *d*-cholestane. The optical activity of the oils is more pronounced as the quantity of unsaturated substances in them diminishes.

Further details of a new crude oil from Papua are supplied by J. Read and A. C. P. Andrews.[10] Previous work demonstrated that the fraction to 170° C. of the Papuan oil contained about 11% of aromatic hydrocarbons, from which a fraction having a combined content of benzene and toluene amounting to about 10% could easily be obtained. The oil thus contains appreciable amounts of aromatic hydrocarbons, although it is less rich in these than Borneo petroleum. The observations now recorded deal largely with the higher boiling fractions.

None of the fractions up to 190° C. (18 mm.) exhibited any measurable optical rotation. Fraction 190°–200° (18 mm.), however, under these conditions gave a dextro-rotation of 0·05°; whilst fraction 200°–225° (18 mm.) gave $\alpha_D = +0{\cdot}10°$ in a 2 dm. tube. Fraction 225°–255° (18 mm.) appeared to possess a small dextro-rotation. Normal tricosane, heneicosane, pentacosane, and heptacosane were identified in the higher fractions.

Among the leading features of this petroleum are absence of pronounced colour or odour in the original oil and in the various fractions; absence of sulphur and nitrogen; and low original specific gravity. Connected with the last feature are the unusually high yield of low-boiling distillates and the small proportion of high-boiling residuals afforded by the oil, the "benzine" fraction (to 150°) amounting to 36%, and the "kerosene" fraction (150°–300°) to 46% by weight, of the crude oil.

PRODUCTION.

A comprehensive survey of the oil resources of the Empire is given by Sir J. Cadman,[11] who states that the production of natural petroleum in 1918 was as follows: United Kingdom 250,000 tons; Canada 40,000 tons; Trinidad 300,000 tons; India 1,150,000 tons;

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[9] *J. prakt. Chem.*, 1920, **101**, 75; *J.*, 1920, 683A.

[10] *J.*, 1920, 289T.

[11] *J.*, 1920, 215R.

Egypt 250,000; Australia and New Zealand 10,000; Sarawak 80,000. The total for the British Empire was 2,080,000 tons; for Persia 1,500,000 tons; whilst the World's production was 70,000,000 tons.

A recent official statement in regard to the progress of the oil-drilling operations during the current year gives information concerning seven borings in Derbyshire, two in Staffordshire, and two in Scotland. In addition to the Hardstoft boring, which still continues to yield seven barrels a day, indications of oil have been found in the Ironville Limestone series. One bore has been suspended. One of the bores (Apedale) in Staffordshire has also been abandoned, but a new one is to be sunk near by. At West Calder (Scotland) a depth of 3844 ft. has been reached after encountering a light show of oil at 3705 ft.[12]

Sir John Cadman[13] has indicated that there is little reason to doubt but that oil in commercial quantities will eventually be forthcoming in the United Kingdom, though it may take years to develop fully.

Norfolk crude shale oil is stated to possess a reddish-brown colour and a garlic odour; its sp. gr. is 0·998, and on fractional distillation it yields 10–20% of gasoline and 40–50% of kerosene, leaving a heavy residue boiling above 270° C. On distilling this residue up to 300° C. there is left a bituminous material which should be of value as a binder in road-making. The average refining loss for Norfolk shale oil is estimated to be about 25%.[14]

Among oil developments abroad, interesting accounts of progress in Western Ontario,[15] Trinidad,[16] Mexico,[17] Philippine Islands,[18] and Echigo (Japan)[19] have appeared; the oil shales of Colorado have also been dealt with.[20]

OXIDATION OF PETROLEUM PRODUCTS.

A problem of constant interest is the synthetic preparation of fatty acids from petroleum and certain of its products; for when an economic method is available for the manufacture of these acids a working basis will be created for the synthesis of edible products. Zelinski has already applied the Grignard reaction to the production of fatty acids from petroleum, and so long ago as 1902 patented[21] a process for the chlorination of certain petroleum fractions, whereby an acid $C_{10}H_{18}O_2$ was obtained which on heating with glycerin at 250° yielded a diglyceride and a triglyceride to the extent of 60% of the theoretical.

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[12] *Mining Mag.*, Oct., 1920.
[13] *J.*, 1920, 195R.
[14] *J.*, 1920, 20R.
[15] *J.*, 1920, 304R.
[16] *J.*, 1920, 95R.
[17] *J.*, 1920, 239R.
[18] *Oil and Gas J.*, 1920, **18**, 66.
[19] *J.*, 1920, 289R.
[20] *J.*, 1920, 57R.
[21] G.P. 151,880.

Some of the best results are said to have been obtained by the oxidation of paraffin for about fifty hours at a temperature of 100°–200° C., mercuric oxide or previously oxidised paraffin being utilised as a catalyst. A somewhat similar method is that of the A.-G. für Mineralölindustrie of Bohemia. It has been stated that this firm has been working on a large scale since 1915, a process which consists mainly in blowing air into melted paraffin for fifteen to eighteen days at a temperature of 130°–135°. The oxidation of paraffin has formed the subject of several investigations during 1920. F. Fischer and W. Schneider[22] heated pure paraffin or crude expressed paraffin with dilute sodium carbonate solution in an autoclave at about 170° C., whilst simultaneously compressed air was pumped through the mixture. The paraffins were oxidised more rapidly under these conditions than at atmospheric pressure, and the yield of fatty acids was as high as 90% of the paraffin used. The rate of reaction varied with the temperature, and was proportional to the pressure of the air. Iron, manganese, and copper had approximately equal catalytic effects but other substances investigated were less active. The highest yields in a given time were best obtained by working to secure complete neutralisation of the sodium carbonate solution rather than complete utilisation of the paraffin. The acids formed were true monobasic fatty acids completely soluble in light petroleum; unlike the commoner members of this series, however, they contain an uneven number of carbon atoms. The following have been definitely identified:—$C_{19}H_{38}O_2$, m.p. 65°–66° C.; $C_{17}H_{34}O_2$, m.p. 58°–59° C.; $C_{15}H_{30}O_2$, m.p. 50°–51° C.; $C_{13}H_{26}O_2$, m.p. 38° C. Examination of a patented process for the oxidation of paraffin by blowing air through the substance heated at 135°–145° C. in an iron vessel in the absence of water showed that the actual products are the acid anhydrides, which can be separated from unaltered paraffin by means of acetone. At the moment there is considerable difference of opinion as to the conditions which must obtain to secure the best yield of acids.

A. Grün[23] found that pure paraffins, or mixtures such as vaseline or petroleum, were readily oxidised under suitable conditions by air or even by gaseous mixtures containing as little as 1% of oxygen. If the conditions of reaction are not carefully chosen, one carbon atom after another of the intermediate products can be oxidised away, and ultimately formic acid or carbon dioxide may be obtained. When oxidation is not too vigorous, the product consists of mixtures of waxes with more or less free acid, alcohols, and some unsaponifiable matter. The composition of the mixture of acids depends on factors such as temperature, duration of action, etc., and the product may consist mainly of the series C_{16} to C_{22} or higher. Hydroxy-fatty acids are also formed and are present partly in the form of esters or estolides, whilst unsaturated acids are present, probably derived from the hydroxy-acids by loss of water. The unsaponifiable matter consists to a small extent of unchanged paraffin, but chiefly of higher alcohols together with other compounds, probably aldehydes, but possibly also ketones."

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[22] *Ber.*, 1920, **53**, 922; *J.*, 1920, 521A.

[23] *Ber.*, 1920, **53**, 987; *J.*, 1920, 521A. *Cf.* Kelber, *J.*, 1920, 220A.

H. H. Franck[24] has investigated the effect of catalysts on the cracking of aliphatic hydrocarbons in the presence of oxygen. Compounds of lead, manganese, mercury, vanadium, and chromium gave good results ; alkalis and alkaline-earths were also satisfactory. A dark expressed residue of paraffin wax yielded 65% of fatty acids in which there were only traces of stearic and arachidic acids. A sample of the mixed fatty acids esterified with glycol in the presence of 3% of sulphuric acid was converted into a solid fat with the odour of coconut oil. When refined this product was pale yellow and had the characters of good edible fat.

C. Kelber[25] also found a manganese catalyst advantageous, and discovered that paraffin, vaseline, and mineral oil distillates may be oxidised rapidly and almost completely by means of a well-divided current of oxygen at 140–150°C. Paraffin wax of m.p. 50°–51° gave 25% of a distillate containing intermediate fatty acids, 40–50% of a residue of higher fatty acids, and 5–10% of hydroxy-fatty acids. The same author[26] investigated the residue obtained by the oxidation of paraffin wax amounting to 90–100% of the original substance. When purified by washing with water and subsequently hydrolysed, it yields a highly complex mixture of fatty acids. The following have been definitely isolated : capric, myristic, palmitic, heptadecoic, stearic, and arachidic acids, and an acid $C_{16}H_{32}O_2$ which is isomeric with palmitic acid and possibly identical with Bergmann's isopalmitic acid. On the other hand, K. Löffl,[27] using a variety of metallic catalysts, found that yields did not differ greatly. The temperature giving the best results was from 115°–120°, and the optimum pressure was three atmospheres. The reaction was assisted by the presence of water.

H. Franck[28] has extended catalytic oxidation to the cases of lignite oils and low-temperature tar oils. The fatty acids obtained were not only excellent for soap making, but could be esterified with ethyl alcohol, glycol, or glycerin, yielding useful edible fats.

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[24] *Chem.-Zeit.*, 1920, **44**, 209 ; *J.*, 1920, 395A.
[25] *Ber.*, 1920, **53**, 66 ; *J.*, 1920, 220A.
[26] *Ber.*, 1920, **53**, 1567 ; *J.*, 1920, 715A.
[27] *Seifens.-Zeit.*, 1920, **47**, 622 ; *Chem.-Zeit.*, 1920, **44**, 561 ; *J.*, 1920, 604A.
[28] *Die Seife*, March 30, 1920 ; *J.*, 1920, 186R.

A different avenue was explored by C. Harries, R. Kœtschau, and E. Albrecht[29] by the application of ozone. The ozonides of unsaturated aliphatic oils derived from petroleum, or from the tar products of lignites, shales, peats, and asphalts, are decomposed, in solution if necessary, with formation of aldehydes or acids. For example, a sample of gas oil from the lignite tar yielded acids, of which the fraction boiling at 180°–200° C. at 10–12 mm. contained solid fatty acids. The acids which were produced ranged from heptoic acid to lauric acid, whilst the residual oil which resisted the action of ozone and of caustic alkali was of value as a lubricant and for use in transformers. Similarly F. Fischer and H. Tropsch[30] have shown that montan wax, suspended in carbon tetrachloride or glacial acetic acid, was changed to a light brown product by the passage of ozone for a short time, and after prolonged treatment products were obtained which were soluble in dilute alkalis. Apparently the wax-esters are decomposed by the action of the ozone with the formation of acids. Montanic acid, which was isolated from the products of the saponification of montan wax, is also attacked by ozone giving acids of lower molecular weight which form typical soaps with alkalis.

It seems evident that the commercial production of fatty acids, if not at the moment a *fait accompli*, is yet near accomplishment. The lower grades of paraffin wax are of little value except as fuel, so that the raw material should be cheap and abundant. Perhaps the most interesting point in connexion with this branch of petroleum chemistry is the relative ease of oxidation exhibited by the saturated paraffins.

NATURAL GAS.

Details are given in Bulletins 178C and 178 published by the Bureau of Mines, Washington, of the helium plants erected during the war. The large scale production of helium is one of the outstanding scientific achievements of the war period. Towards the end of 1917 it was decided to erect experimental plants working the systems of Linde, Claude, Norton and Lacy for the production of helium from natural gas. The Norton process represents the latest practicable development in liquefying and separating gases, and the " Argon " Plant No. 3, that was completed October 1, 1918, operating on this process, gave an estimated production of helium of 30,000 cb. ft. per day. Plant No. 1 (Linde) and Plant No. 2 (Air Reduction) had respective capacities of 5000 and 3000 cb. ft. per day. Altogether 200,000 cb. ft. of helium of 92·5% purity was produced by Plants 1 and 2. It is anticipated that helium of the highest purity will be produced by Plant No. 3 in quantity very shortly, and further experimental work is to be carried out on this system. Helium, which in pre-war days cost about \$2000 per cb. ft. to produce, can now be produced on the large scale at an approximate cost of \$0·7 per cb. ft.

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[29] G.P. 324,663 ; *J.*, 1920, 765A.

[30] *Ges. Abhandl. zur Kenntnis der Kohle*, 1919 II. 162 ; *J.*, 1920, 55A.

J. C. McLennan[31] gives further details respecting the occurrence and isolation of this gas. The gases from some springs in France have been shown to contain as much as 5% of helium; natural gases in the Western States of America contain 1–2%, but within the British Empire no natural gases have been found to contain as much as 0·5%. Natural gases from Ontario and Alberta, Canada, were found to be richest in helium (0·34% and 0·33% respectively), and it was estimated that these sources could supply from 10 to 12 million cb. ft. of helium per annum. Gases from New Brunswick were found to contain 0·064%, and the richest natural gases in New Zealand not more than 0·077%. A natural gas from Pisa, Italy, contained no helium; the gas at Heathfield, Sussex, 0·21%; that from the King's Spring, Bath, 0·16%; and the natural gases at Pitt Meadows, Fraser River Valley and Pender Island, on the Gulf of Georgia, British Columbia, were ascertained to possess a nitrogen content of over 99%.

By suitably modifying the Claude oxygen-producing column it was found that helium of 87–96% purity could be regularly and continuously produced. Ultimately an auxiliary apparatus was added whereby the purity of the gas was raised to 99% or higher. From the experience thus obtained, it was possible to draw up specifications for a commercial plant to deal with about 56,500 cb. ft. of gas per hour at normal temperature and pressure.

According to a report presented by V. H. Manning,[32] all the sources of natural gas containing helium in the United States can produce a total of 3 million cb. ft. per day of gas containing over 0·35% of helium for a period of from 2½ to 3 years. The field most suitable for working is stated to be at Petrolia, Texas, although helium has been found in Kansas, Oklahoma, Ohio, California, and Wyoming.

The removal of volatile hydrocarbons from natural gas has become one of the most promising methods for the increased production of motor fuel. It is probable that not a tithe of the potential yield of casinghead gasoline has been exploited. The absorption method appears likely to become the standard system of treatment, and a recent bulletin of the Bureau of Mines deals very fully with existing technique. A useful compendium is given by R. P. Andrews[33] in which the principles underlying the compression, refrigeration and absorption methods of recovering gasoline from natural gas are enunciated and the applications of the different methods are discussed. Communications on natural gas from the standpoint of the fundamental physico-chemical data are published by J. Satterly and his co-workers,[34, 35, 36] whilst the heating value of a casinghead gasoline is discussed by R. P. Anderson.[37]

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[31] *J.*, 1920, 252R.

[32] *J.*, 1920, 288R.

[33] *J. Ind. Eng. Chem.*, 1920, **12**, 547.

A method of analysis of natural gas for its gasoline content has been worked out by R. P. Anderson and C. E. Hinckley,[38] who use highly activated gas-mask charcoal (8 to 14 mesh) as an efficient absorbent of the light spirit. The gas is passed through two glass tubes about 0·8 in. in diam., each containing about 8 in. of charcoal. The gasoline may be recovered by covering the charcoal with mineral oil and distilling. The utilisation of activated charcoal as a means of extracting gasoline on the commercial scale is discussed by G. A. Burrell, G. G. Oberfell, and C. L. Voress.[39] The process consists in bringing the gas into intimate contact with activated charcoal, whereby the recoverable vapours are retained and the denuded gas is allowed to return to the distribution lines. A charcoal plant costs less to install, is cheaper to operate, and produces more and a better grade of gasoline than do compression or oil absorption plants. Charcoal made from coconut shells by the steam activation process which was developed during and since the war appears to be the best suited for this purpose.

FUEL OIL.

The utilisation of mixtures of powdered coal with fuel oils was touched upon in last year's report. Since then L. W. Bates[40] has published his views on this matter, without, however, adding materially to what was previously known or surmised. Colloidal fuel as defined by Bates is "a stable, mobile, atomisable fuel displaying colloidal characteristics, comprising particles of solids, droplets of liquids or minute bubbles of gases, or combinations thereof, suspended in one or more varieties of liquid hydrocarbons." The particular colloidal fuel discussed consists of a suspension of coal in petroleum residuum, the stability of the suspension being maintained (1) by means of a "fixateur," which may be soap solution or lime-rosin greases; or (2) by "peptising" the mixture by adding to it a definite proportion of coal distillates, such as tars and the middle fractions; or (3) by grinding the solid substances so that about 97% will pass through a 200-mesh screen. The author

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[34] J. Satterly, *Trans. Roy. Soc. Canada*, 1913, **13** (III.), 109.

[35] H. A. McTaggart and E. Edwards, *Trans. Roy. Soc. Canada*, 1919, **13**, (III.), 57.

[36] J. Satterly and J. Patterson, *Trans. Roy. Soc. Canada*, 1919, **13** (III.), 123; *J.*, 1920, 539A.

[37] R. P. Anderson, *J. Ind. Eng. Chem.*, 1920, **12**, 852; *J.*, 1920, 683A.

[38] *J. Ind. Eng. Chem.*, 1920, **12**, 735; *J.*, 1920, 621A.

[39] *Chem. Age (N.Y.)*, 1920, **28**, 347.

[40] *J.*, 1920, 395R.

claims that by one of these methods it is possible to suspend 55% of solid material in the liquid ingredient, samples of the fuel containing 42% of mixed coal and coke having remained perfectly stable after 8 months' storage. The addition of carbonaceous particles to an oil, and the proper association of the components, is said to raise materially the flash-point of the oil, and reduce the evaporation. Owing to this property the U. S. National Board of Fire Underwriters gives colloidal fuel preferential rating over plain fuel oil. It is further claimed that colloidal fuel has a higher calorific power than either of its principal constituents separately.

More complete details are given by H. Plauson,[41] who recommends the treatment of 30 parts of the finely-divided substance with 70 parts of the dispersive agent for a certain time, followed by dilution with suitable quantities of the agent, and thorough mixing. For the preparation of "liquid coal" the coal is finely ground and emulsified for half to three hours with 60–70% of neutral tar oil, peat oil, animal or vegetable oils, etc., at a very high velocity and for a shorter time if protective colloids are added. In Block's "colloid mill" the mixing is effected in globular vessels which revolve eccentrically at an excessively high speed and fling the mixture against baffle bars, while if desired, the vessels may be heated or cooled.

From the point of view of an accurate terminology it is perhaps unfortunate that the term "colloidal" has been attached to these mechanical mixtures.

Pitch is brought into a stable fluid suspension by means of a method described by F. Tinker.[42] A fuel oil containing both mineral oil and tar or tar oils containing pitch is obtained by adding to the tar etc., before it is mixed with the mineral oil, a third ingredient or intermediate oil which is miscible with each of the other ingredients and which is intermediate to them in its chemical composition and surface tension and other properties.

W. R. Ormandy[43] has drawn attention to the demand for motor fuel which now amounts to 1,000,000,000 gallons per year, representing about 15,000,000 tons of crude oil based on the somewhat high yield of 20% petrol. Examination of the Patent Office files during the years 1913-1919 indicated that the attention of inventors was being increasingly given to blends of volatile fuels, alcohol being assumed to be a component of the motor fuel of the future. It is well known that commercial alcohol requires a third liquid before it will mix with the straight-run petrol distillates. Fusel oil or a higher carbinol was suggested as the menstruum in a 1913 patent. In the next year ethyl ether was put forward as a means of increasing the vapour tension of motor-alcohol, the more volatile component being incorporated to the extent of about 10%; whilst later it was proposed to increase the ether content to 40 or 60%. The well-known blend "Natalite" is approximately a 50% by weight mixture of alcohol and ether, containing ammonia or trimethylamine to overcome the alleged tendency of alcohol to cause corrosion. The granting of patents which protect blends of inflammable volatile liquids was criticised on the grounds that such blends are known to be possible motor fuels by the chemist and engineer.

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[41] *Chem.-Zeit.*, 1920, **44**, 553, 565; *J.*, 1920, 589A.

[42] E.P. 130,699; *J.*, 1919, 711A.

[43] *J.*, 1920, 90R.

Lubrication and Lubricants.

The *rationale* of lubrication has been thoroughly discussed during the past year, conferences specially devoted to the object have been held, and the Department of Scientific and Industrial Research have published the finding of the Committee appointed to study the question. This report, which is too voluminous for more than a passing notice and too important for mere abstracting, should be closely considered by petroleum chemists and engineers. The bibliography on the chemistry, physics, and engineering aspect of lubrication will be issued at a later date (*cf. J.*, 1921, 36A, 37A).

An important paper by R. M. Deeley on "Oiliness and lubrication"[44] indicates that in recent years the property of "oiliness" has become associated with the presence of unsaturated compounds, which constitute 20–40% of most lubricating oils Hardy (*J.*, 1919, 7T) concluded "that lubrication depends wholly on the chemical constitution of a fluid," and that "the true lubricant is always a fluid which is absorbed by the solid face." Deeley measured static coefficients of various oils between metals. When no lubricant is used the static coefficient increases as the surfaces continue to rub against each other. Such clean surfaces are very sensitive to contamination influences, *e.g.*, moisture. It is interesting to note that the oils which have the smallest coefficient of friction are those which have proved the best lubricants in practice It would appear that the unsaturated molecules of the lubricant enter into a firm physico-chemical union with the metallic surfaces forming a friction surface which is a compound of oil and metal This surface would also appear to be of more than molecular thickness. Thin films of this kind cannot be removed by merely wiping, but must be ground off under water, or a thin layer of meta must be cut off.

During the year J. E. Southcombe and H. M. Wells have continued the development of their views on the influence of smal amounts of fatty acids when dissolved in mineral oils.[45] These authors have emphasised the distinction between the lubrication of fast-running shafts with a large excess of oil, where the frictional values are a function primarily of the oil viscosity, and that of slow-speed machinery with high bearing pressure, where viscosity measurements no longer assist in the choice of the lubricant. It was found that the interfacial tension against water of vegetable and animal oils was very much lower than that of a mineral oil, and this lowering was due to the slight content of free fatty acid in the fatty oils ; by removing the free fatty acids from the saponifiable oils the tension rises, and by adding free fatty acids to the mineral oil the tension can be lowered. It follows that if a substance be added to an oil which brings about a lowering of interfacial tension, such addition will act favourably as far as lubrication is concerned by preventing a rupture of the liquid film and consequent direct contact between the metals. In point of fact, Archbutt concludes from experiments which he has recently communicated to the Physical Society that the addition of 1% of free fatty acids to a mineral oil lowers the frictional coefficient to the same extent as does 60% of pure rape oil, and thus lends support to the authors' contention that it is not the glyceride, but the free fatty acid in a compounded oil which improves its lubricating value. The authors' theory that the action of the fatty acid is due to the fact that the interfacial tension between oil and water and between oil and mercury is greatly lowered by the addition of fatty acid to a mineral oil has met with criticism, and it has been pointed out that, although neutral rape oil added to mineral oil greatly reduced the friction coefficient, the interfacial tension between neutral rape oil and water was nearly as high as that between mineral oil and water. In the lubrication of a shaft or journal running at a fairly high speed and under moderate pressure, the bearing is separated from the journal by a film of oil, and the friction is solely due to the viscosity of the lubricant. That property of a lubricant which is not viscosity and is termed " oiliness " only becomes important when the conditions are such that solid or " contact " friction occurs, and all recent work points to the fact that it is the chemically reactive and unsaturated constituents of lubricants which promote " oiliness," and that they do so by entering into physico-chemical union with the solid faces lubricated, forming new composite surfaces which lower surface energy and opposing less resistance to shear than the unlubricated surfaces. The greater activity of free fatty acids is quite in accordance with this theory.

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[44] Phys. Soc., Nov. 28, 1919; *Engineering*, 1919, **108**, 788; *J.*, 1920, 57A

[45] *J.*, 1920, 51T, 47R, 53R.

Further discussion of Wells and Southcombe's work occurred at the British Association Meeting[46] in connexion with a symposium on " Lubrication." Dunstan and Thole, dealing with the chemical nature of heavy mineral oil, brought out the point that the " unsaturated " components of lubricating oil were removable by means of sulphuric acid; that they possessed iodine values which steadily increased with the concentration of Wijs' reagent and with time, but were unaffected by hydrogen in conjunction with nickel catalyst. They suggested the possibility of the presence of closed saturated rings which were opened up under the influence of acid and iodine chloride. Tizard discussed the nature of lubrication from the point of view of adsorption phenomena, and criticised Southcombe's falling-drop method of measuring interfacial surface energy, pointing out that when mercury fell through castor oil the droplets did not coalesce, whereas through glycerol of the same viscosity and drop number coalescence was observed.

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[46] *J.*, 1920, 300R.

A memorandum on "Solid lubricants," by T. C. Thomsen and L. Archbutt has been issued by the Department of Scientific and Industrial Research. With properly lubricated bearings the chief advantage of using a solid lubricant is apparently the effect on the friction at the moment of starting. Flaked graphite is stated to build up a surface on very rough bearings, but it may be detrimental where small clearances exist. Colloidal graphite would appear to be a useful solid lubricant were it not for the fact that it is very susceptible to the flocculating action of electrolytes; in fact, less than 0·1% of free fatty acids is sufficient to precipitate it.

Amongst new lubricating media may be mentioned the synthetic oils described by R. H. Brownlee.[47] A hydrocarbon oil of high flash-point and viscosity and low cold test, suitable for lubrication, s obtained by polymerisation of light unsaturated hydrocarbons by agitating them with a catalyst preferably at 200°–400° F. As catalysts, anhydrous aluminium chloride, or a halide, or reagents which produce a halide in the nascent state are used. The oil, after treatment, is washed and distilled with steam. The distillates nclude products having the flash points of naphtha and kerosene, and a variety of lubricating oil fractions.

C. Francke[48] has suggested the purification of naphthenic acids by means of a mixture of fuller's earth and sulphur dioxide. The filtrate is heated after addition of nickel formate and subjected to the action of hydrogen, whereby a lubricating oil is produced.

The Allgemeine Ges. für Chem. Ind. m. b. H.[49] applies the Edelanu process to hydrocarbons from which the lubricant is to be made.[50] The insoluble fraction is used as a lubricant. It is now laimed that the soluble portion is applicable for certain purposes s a highly viscous lubricant after the removal of a small amount f SO_2 contained therein. For this purpose a current of air is conducted through the oil after it has been heated for a long time under reduced pressure, whilst a current of dry ammonia gas is introduced, to neutralise the acids still present.

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[47] E.P. 141,753.

[48] G.P. 324,227; *J.*, 1920, 776A.

[49] G.P. 315,389.

[50] G.P. 287,309.

CRACKING.

The more euphonious term "pyrolysis" has been suggested by W. A. Hamor to replace the more familiar expression used as the heading of this section. Papers dealing with the general aspect of the subject have appeared by F. W. Padgett[51] and Y. Nakazawa.[52] Padgett deals firstly with the general principles of the production and refining of cracked gasoline and then with the proved commercial processes including those of Burton, Greenstreet, and McAfee. Nakazawa points out that the generally recognised defects in nearly all methods of cracking petroleum now in use are: (1) an accumulation of carbon especially in the case of manufacture of aromatic groups, (2) loss of oil as fixed or permanent gas, (3) poor yields, and (4) the formation of impurities. To guard against the accumulation of carbon the use of several cracking tubes in succession is described. The use of copper or copper-lined tubes is beneficial, but iron tubes are to be avoided. The use of ferric oxide or copper oxide in the tube will prevent liberation of carbon by hydrogenation, whilst the formation of fixed gas will be correspondingly minimised.

There is little to chronicle respecting new cracking processes. A. M. McAfee (*vide* Dunstan, E. P. 119,751) has applied aluminium chloride to the refining of pyrolytic gasoline.[53]

C. Cordes[54] has shown that heavy hydrocarbons, such as heavy raw mineral oils or residues, are converted into lower-boiling products by distilling them with hydrosilicates. On similar lines C. F. Thiebe[55] mixed crude oil with an equal amount of fuller's earth and digested the mixture at 100°. The oil obtained by this process was light green in colour while the original crude had a brownish black, opaque appearance. The earth was washed with gasoline and then extracted. The extracted matter was found to be 9·8% of the original oil and consisted of phenoloid substances, yellow resinous compounds, and black asphaltic matter. Yields of gasoline are increased by this treatment of crude from 11 to 43% depending on the crude oil treated. Dark coloured oils distilled with clay yield 1·3% of water, probably formed by the decomposition of the oxygenated compounds in the oil. This water contains free sulphuric acid, naphthenic acids, and nitrogen compounds.

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[51] *Chem. and Met. Eng.*, 1920, **23**, 521, 908.

[52] *J. Chem. Ind., Tokyo*, 1919, 394.

[53] U.S.P. 1,333,072; *J.*, 1920, 149A.

[54] E.P. 147,648.

[55] *Petroleum Age*, 1920, **7**, [2], 45.

F. Bergius[56] successfully hydrogenated heavy hydrocarbon oils at 100 atm. pressure with hydrogen at a temperature of about 400° C., and has effected their conversion into light oils. Metals, metal oxides, or hydroxides may be mixed with the oil during the hydrogenation to bring about simultaneous desulphurisation and to accelerate the hydrogenation.

An operation, the inverse of cracking, is suggested by W. North.[57] Paraffin oil, or heavy oil from which solid paraffin has been removed, is heated under pressure with finely-divided gas-coke at 300° C. Copper oxide may be added to remove the liberated hydrogen. It is stated that the product contains 20% of soft paraffin.

The formation of resin from cracking spirit is only too common an occurrence from the refiners' point of view, but E. H. Leslie and C. Barbre[58] obtain a synthetic resin from cracked oil by heating with a porous catalyst such as coke, charcoal, fuller's earth, or kieselguhr, filtering off the catalyst, and separating the oil from the resins.

REFINERY TECHNIQUE.

The two tendencies apparent in modern refinery practice lie in the direction of economy of heat and manipulation in distillation and in the elimination of the barbarous and mediæval treatment of distillates by means of acid and soda.

In a very valuable Bulletin (No. 162) of the Bureau of Mines, J. M. Worksworth deals with the removal of the lighter hydrocarbons from petroleum by continuous distillation, especial reference being made to plants in California. The methods of constructing and operating types of topping and skimming plants representative of those used in the United States are presented in detail. Tables, curves, drawings and illustrations are given freely.

The difficulties in the way of making sharp cuts when distilling petroleum are discussed by S. Masfaraud,[59] who shows that when the mixtures are very complex the products are only roughly fractionated by distillation. Some separation is certainly effected, but it is necessarily very imperfect, for if the most volatile products predominate in the vapours, they are accompanied by very heavy products. The fractionation can never be more than relative, *i.e.*, the final mixture will be a little less complex than the initial one.

A frequent refinery trouble is the corrosion of petroleum condenser-tubes. M. Freund[60] has shown that condenser tubes are attacked rapidly in the portions over which the condensate flows and particularly at the place where the vapour line passes into the condenser box. Free carbon dioxide was found in all oil fractions and may be of importance in the corrosion of tanks and columns. Traces of sulphuric acid and sulphates but no organic acids were detected in the condensed water. Similar occurrences were met with by R. R. Mathews and P. A. Crosby[61] who showed that when petroleum which contained brine, with magnesium chloride as one of its constituents, was distilled in pipe stills, hydrochloric acid was evolved by hydrolysis, and in consequence serious corrosion took place in the fractionating system and in the condensers. As it is desirable to prevent, if possible, the rapid corrosion caused by the hydrochloric acid produced, several different methods have been investigated, and this paper covers some of the results obtained. Anhydrous ammonia was successfully tried as a neutralising agent. Ammonia cylinders were connected with the vapour line, just after the vapour left the stills, and before it reached the first dephlegmator. Before using the ammonia the tubular condenser was in use for approximately 100 days before it was necessary to replace any tubes, but after using ammonia the life of the system was trebled.

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[56] G.P. 304,348 ; *J.*, 1920, 222A.

[57] G.P. 319,123 ; *J.*, 1920, 566A.

[58] U.S.P. 1,337,523 ; *J.*, 1920, 440A.

[59] *J.*, 1920, 302T.

[60] *J.*, 1919, 808A.

The same authors[62] showed that an Oklahoma oil gave a condense water containing 0·012 g. of hydrogen chloride per litre of oil. The acid content was traced in this case also to the hydrolysis of magnesium chloride in the brine which accompanies the crude oil.

A series of investigations in which fuller's earth and other adsorbent bodies are proposed as refining agents is noteworthy. W. C. Phalen[63] observes that the bleaching action of fuller's earth on mineral oils is independent of its chemical composition, and depends on its power of selective absorption. The following factors are important: The longer the column of earth the better the bleaching effect; the coarser the earth the more rapid the flow and the poorer the bleaching effect. Filtration should, therefore, take place at the lowest temperature compatible with the fluidity of the oil.

J. J. Hood[64] proposes to desulphurise straight-run distillates by vaporising and bringing the vapour into contact with granular alumina or ignited magnesite at a temperature below the boiling point of sulphur. The hydrogen sulphide resulting from the dissociation of the sulphur compounds may be absorbed in any usual manner.

The Hall Motor Fuel, Ltd., and T. A. McCrea[65] adopt similar means but at a lower temperature (150°–300°), whilst T. T. Gray[66] with the object of reducing the quantity of unsaturated compounds in cracked gasoline or similar hydrocarbon oils, passes the material in vapour form, through a mass of fuller's earth, bone-black, charcoal or similarly acting substance which is heated to a temperature above the boiling point of the oil.

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[61] *Chem. and Met. Eng.*, 1920, **22**, 1122.

[62] *Chem. and Met. Eng.*, 1920, **22**, 491.

[63] *Chem. and Met. Eng.*, 1919, **21**, 469; *J.*, 1920, 67A.

[64] E.P. 145,818; *J.*, 1920, 651A.

[65] E.P. 141,272; *J.*, 1920, 396A.

[66] U.S.P. 1,340,889; *J.*, 1920, 651A.

The utilisation of acid tar forms the subject of communications. R. W. Albrecht[67] uses the washed residue together with Trinidad asphalt as material for paving, whilst according to E. A. Kolbe[68] about 90% of the sulphuric acid in the waste acids from lubricating oil refining may be recovered in the form of sulphur dioxide by heating the waste acid. The use of alcohol for removing sulphuric acid or its products is described by Z. Budowicz[69] who treats the oil after acid washing with 0·25–0·3% of alcohol. In this way 7% of sulphonic acids have been produced from Baku solar oil. These possess valuable detergent and emulsifying properties.

The technique of wax manufacture is discussed by K. Fuchs[70] and by A. Czekely[71] who indicate the best conditions for crystallisation and for sweating.

COLLOID CHEMISTRY OF PETROLEUM.

The Third Report of the Committee on the general and industrial applications of colloid chemistry[72] contains a section on the colloid chemistry of petroleum which, *inter alia*, deals with viscosity-hysteresis effects in paraffin-containing oils ; coagulation of asphaltic substances during acid treatment ; adsorption of sulphur-containing compounds and colouring matter on fuller's earth, bauxite, and the like ; the colloid state of Trinidad asphalt and its bearing on road making ; the treatment of emulsions ; colloid fuel oil ; lubricating oils considered as iso-colloids, and the refining of wax.

The presence of colloidal clay in Lake asphalt is alluded to in a paper by H. S. Miller.[73]

New technical methods for separating aqueous oil emulsions are described by I. Móscicki and K. Kling.[74] Aqueous mineral oil emulsions may be separated by maintaining them under pressure at a somewhat elevated temperature.

Oilfield emulsions are dealt with by J. L. Sherrick.[75] The emulsions occurring in the Goose Creek field (Texas) consist of salt solution as disperse phase and oil-containing asphalt as the dispersing phase. The water particles are negatively charged, as is shown by their moving towards the anode when subjected to a suitable potential gradient. Strongly adsorbed cations neutralise the charges on the water particles. Both ions of an added ferric salt are effective in precipitating the water particles, whilst addition of ether decreases the stability of these emulsions by dissolving some of the asphalt. Suitable treating compounds for breaking oil-field emulsions are hydrophile colloids (crude soaps or sodium salts of sulphonated coal tar or petroleum).

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[67] *Chem.-Zeit.*, 1920, **44**, 282 ; *J.*, 1920, 358A.
[68] *Petroleum*, 1919, **14**, 837 ; *J.*, 1920, 438A.
[69] *Przemysl Chem.*, 1920, **4**, 63 ; *J.*, 1920, 740A.
[70] *Petroleum*, 1919, **14**, 128, 191, 285 ; *J.*, 1920, 220A.
[71] *Petroleum*, 1919, **15**, 109 ; *J.*, 1920, 438A.
[72] Dept. Sci. and Ind. Research, 1920.
[73] *Chem. and Met. Eng.*, 1920, **22**, 749.
[74] *Przemysl Chem.*, 1920, **4**, 2 ; *J.*, 1920, 741A.
[75] *J. Ind. Eng. Chem.*, 1920, **12**, 133 ; *J.*, 1920, 289A.

ORIGIN OF PETROLEUM.

In a series of optical investigations on some primary South American petroleums, E. Longobardi[76] observed that petroleum obtained from Devonian rocks, that is to say, from a level which corresponds with the oldest of the sub-Andean deposits, gave no fractions which showed rotatory power. This he regards as opening anew the question as to whether optical rotatory powers are solely conferred by the passage through strata containing active organic substances.

The experiments of A. Pictet and J. Potok[77] confirm the theory of Engler in so far as the acyclic constituents of petroleums are concerned, and even extend the theory to cover the genesis of the hydrocarbons in paraffin wax. This latter material seems to be the primary product of the decomposition of fats, and should not be considered as arising from the condensation of simple hydrocarbons. The authors consider that naphthenes are products of a slow decomposition of optically active compounds which pre-existed in the vegetable material.[78] Petroleums have not had a common origin, and no single theory can account for the genesis of all types. It is certain that petroleums of the character of Pennsylvania crude have been derived by a process of slow decomposition from fats. The resinous or terpene-like substances of the higher plants are probably the source of naphthenic crudes. The constituents of crudes of mixed types have probably been formed simultaneously from the two classes of substances.

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[76] Soc. Argentina Cienc. Nat.; *Chem. Abs.*, 1920, 1604.

[77] *Helv. Chim. Acta*, 1919, **2**, 501; *J.*, 1919, 939A.

[78] *Ann. Chim.*, 1918, **10**, 249.

COLOURING MATTERS AND DYES.

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The Advisory Committee of the Colour Users' Association proceeded to Germany in January, 1919, to purchase supplies of dyes required by British consumers in addition to the dyes received under the Reparation Clauses of the Peace Treaty and succeeded in buying 140 tons, but as the unexpected Sankey Judgement rendered possible the free importation of German dyes, the policy of collective purchase was abandoned within a few months.

The figures available with regard to the output of dyes in the German factories provide an interesting study, for whereas in February the total production was 1600 tons, or approximately 10% of their pre-war capacity, this production steadily increased to 2400 tons in March, 3300 tons in April, 3800 tons in May, 4800 tons in June, and 5500 tons in July. The increase, moreover, was not in those colours, such as vat dyes and fast alizarin dyes, which were particularly desired by our consumers, and of which 228 tons was produced in May and 272 tons in July, but in the bulk colours, such as indigo, direct cotton dyes, acid dyes, and sulphide dyes, which, in the majority of cases, our own manufacturers were capable of producing.

During the first eight months of the year 4687 tons of dyes (the total for 1919 amounted to 3234 tons) and 1480 tons of intermediates, representing a value of £4,089,922, were imported into this country. The dyes imported from Germany alone in the first six months of the year amounted to 387 tons, which included 150 tons of reparation dyes, whilst in the first nine months of the year the figure increased to 1574 tons, of which 877 tons were reparation dyes, and it was pointed out at the end of October that our imports of dyes from Germany amounted to 40% of the 1913 figure, whilst in addition the dyes received from Switzerland considerably exceeded the quantity imported in 1913.

The British colour industry naturally was alarmed at the position, which was largely due to the supineness of the Government, and the controversy which arose as to the best method for the protection of both dye manufacturer and consumer, whether by means of the prohibition of the importation of dyes except under licence, or by a protective tariff, or by a Government subsidy to the dye manufacturer, once again brought the whole matter to the notice of the public.

In the endeavour that was made to find a formula acceptable to both parties which would permit the Government to redeem its pledges, it was unfortunate that whilst the dye manufacturer knew what he wanted, the opinions of the dye users were divided, owing to the diversity of the requirements of the various sections of the industry, and as both parties appeared to regard the matter mainly from a tradesman's standpoint, it was difficult to distinguish between facts and interested propaganda. Arguments based on the respective national values of the dye industry and the textile industry were rather puerile, for by this time it appears that all are agreed that the permanent establishment of the former is essential to our national safety, and that this must be accomplished with as little injury as possible to the interests of the latter, as we receive from that source such a large proportion of our national income.

Proposals to impose a tariff on imported dyes were futile in view of the rate of exchange with Germany, and in the absence of either the restriction of imports under licence or of a subsidy it appeared that the British colour industry would succumb to competition in the present state of its development, for the change over from war to peace conditions was not effected without reorganisation with its concomitant expense and dislocation, the cost of wages and materials has risen continuously, and there has been further delay in the delivery and installation of plant.

The British consumer appears to take exception to one of the great advantages of a licensing system, which is that where dyes pass through a Central Importing Agency contact between the foreign manufacturer and the consumer is avoided, and consequently the former can force no bargain upon the latter with regard to future supplies in return for a supply of some urgently needed dye. In fact, the British consumer appears to overlook the fact that he has been better supplied with dyes during a period of world shortage than has been the case in any other country, for critics consider that past experience has shown unequivocally that access to the most economical, the newest, and the best dyestuffs is impossible under a licensing system, but as the system was in operation during a period when an adequate supply of the best dyes did not exist, the colour manufacturer could scarcely be blamed for lacking faith in the proposal that the sounder policy was to trust to the good sense of the consumer in this country. It is true that the British Alizarine Co. is an outstanding example of how, with good management and the support of the large consumers, the Germans can be fought successfully without Government intervention, but international exchange was not in its present condition during the establishment of this firm and, moreover, the real point at issue was the necessity of a self-contained dye industry in this country which would produce eventually a complete range of dyes of all classes, and not merely an industry which would produce a limited section of dyes.

In any case the production of the standard pre-war dyes is by no means the ultimate object of the British colour industry, for the nation that plays the most important rôle in new achievements is the one which will eventually triumph, and to this end organised research, which might well be subsidised by the Government, is essential. In this connexion A. G. Green has pointed out that "the research laboratories of the British Dyestuffs Corporation are not only centres of investigation where new processes are discovered and old processes are improved, but are also educational institutions where the young chemist fresh from the University can receive a specialised training in colour chemistry to fit him to take his place in the works as a dyestuff technologist." Under present conditions it is to be regretted that the expert staff of the colour works should feel compelled to deal largely with the educational side of the matter, particularly when laboratories exist in other institutions where at least part of this specialised training could be carried out effectively, with the result that our resources would be utilised more completely for the solution of the problems of the moment. The Chemical and Dyestuffs Traders' Association was informed by the President of the Board of Trade in November that no useful purpose would be served by calling a conference to consider the dyestuffs problem in all its bearings and to discuss future legislation. Such an attitude was difficult to understand for what appeared to be needed was an expert commission to investigate the whole question and report on the full facts and merits of the case, while a temporary measure establishing a system of prohibition of imports except under licence was introduced to cover the period of enquiry. However, it was reported on November 25 that the dye manufacturers and consumers were agreed on a common policy for the protection of the dyestuffs industry, although the Calico Printers' Association denied that any real agreement existed among the consumers.

The Dyestuffs (Import Regulation) Act, 1920, was then brought in by the Government and the second reading of the Bill was carried by a large majority on December 7, in spite of the contention that it combines the greatest amount of interference with the textile trade with the least guarantee of encouraging the development of the dyestuffs industry. The Bill, unless it is amended, provides for the prohibition of the importation of dyes and intermediates for a period of ten years except under licence granted by the Board of Trade, advised by a committee consisting of five epresentatives of the dye users, three representatives of the dye nanufacturers, and three other persons not directly concerned, ne of whom shall act as chairman. In the controversy which has aken place, consideration of the problems of the dyestuffs manufacurers in this country too frequently has been confined to the point f view of the British Dyestuffs Corporation, and the fact that here are other important colour producers has been largely overooked. It is, however, greatly to be hoped that the future will see a nore cordial co-operation among British colour manufacturers vhich, while allowing full scope for individual effort, will enable a nore united front to be presented to foreign competition, for there s no doubt that German colour manufacturers place considerable eliance upon the lack of cohesion which exists among the British nanufacturers.

An aspect of the future which must be taken into consideration, lthough not urgent at the moment, is the prospect that at no listant date the world may be over-supplied with dyes, for whilst he German organisation is capable of producing three-quarters f the world's pre-war requirements, Great Britain, America, Switzerland, and France are making efforts, not only to supply heir own needs, but to create an export trade.

British dyes have been well received in the East but the quantities vailable have been utterly inadequate and German manufacturers re recovering their hold on this market.

Some instances of the progress made by individual British manufacturers during the period under review may be quoted.

British Dyestuffs Corporation, Ltd., have increased their range of products by some thirty dyes, which include wool colours such as the Solochrome Blacks, Milling Scarlet 3B, and Disulphine Blue, direct cotton colours of blue, brown, and black shades, basic colours such as Rhodyle 4G, Turquoise Blue G, New Methylene Blue S, lake products such as Monolite Fast Scarlet R, Lake Scarlet 3B, and Naphthol Green, and paper products such as Blackley Fast Scarlet and Duranthrene Blue RT.

Messrs. L. B. Holliday & Co., Ltd. have added over twenty dyes of all classes to the series of colours which they produce in bulk, and have made improvements in the standard of their products; for example, the brands of Safranine are of a quality fully equal to any pre-war type. This firm regard the present trade depression as affording an opportunity for the more rapid multiplication of the number of individual dyes which they are prepared to produce than the demand for their established products has permitted in the past.

Scottish Dyes, Ltd., anticipated that a range of twenty-two valuable colours, including four vat dyes not previously marketed, would be produced in the new works at Grangemouth during this year, but the delay in the building trade in Scotland has hampered progress and only a few of these dyes have been available. It is confidently anticipated, however, that the full demands of the British consumer in vat and acid alizarin colours will be met in the Spring of 1921. This firm has made remarkable progress and has manufactured several of these important colours in larger bulk than the total pre-war imports to Great Britain.

Large extensions to the colour producing plant have been made by the Clayton Aniline Co., Ltd., and this firm is now equipped for the manufacture of a number of colours not previously made in this country. Included in the new ranges are a number of Ciba vat colours, fast chrome colours for wool dyeing, and a large number of direct cotton colours which are being manufactured in increasing quantities.

The admirably laid out and equipped new works of the British Alizarine Co., Ltd., at Trafford Park, are rapidly approaching completion and will be ready to commence production in 1921. The necessary research department has been in existence for some time past.

Messrs. H. N. Morris & Co., Ltd., although chiefly concerned in the refining of coal-tar products, are now manufacturing benzoic acid and benzaldehyde on the large scale, together with a few dyes.

Messrs. Hickson & Partners, Ltd., have continued to extend their works, and amongst new plants erected and put into operation are a reduction building and a modern vacuum distillation plant. This firm is directing increased attention to the manufacture of dyes, and rosaniline base and Magenta are now produced on an extensive scale.

Considerable progress has been made in America and the efforts to establish an export trade in dyes have met with such success that the figures for April, for example, were more than double those for the corresponding month in 1919. The amalgamation of five of the large works in America to form a combination with a capital stated to amount to £60,000,000 has been reported and indicates the determination to make a bid for supremacy in dyestuff manufacture. Legislation of a protective character has been drafted, and a Bill is now before the Senate to establish a system of prohibition and licence. The problem of an adequate supply of anthracene still remains unsolved, although the output has been increased. The difficulty is not primarily the small percentage of anthracene in the tar, nor purely technical difficulties in its recovery, but the fact that its removal leaves the pitch so hard that it does not find a market under American conditions and consequently the anthracene obtained would be so expensive that dyes derived from it could not be made on a competitive basis.

In 1913 less than 7·5% of the dyes used in France were manufactured in that country, whilst to-day more than one-half the dyes used are home manufactured, and of that quantity more than 60% is manufactured by the Compagnie Nationale de Matières Colorantes et de Produits Chimiques. The plans for the establishment of a national dye industry in Sweden have met with no success and the early liquidation of the company, A. B. Svensk Färgämnes Industri, founded in 1917, is anticipated.

INTERMEDIATES.

Sulphonation.

According to a process patented by F. C. Sutton,[1] an aromatic hydrocarbon and sulphuric acid are charged through atomisers, opposed and in close proximity to one another at the upper end of a steam-jacketed tower, provided with a condenser. The reaction product flows down baffle plates and is drawn off at the bottom of the tower, whilst any condensed hydrocarbon is returned to the charging apparatus. In a plant suitable for the sulphonation or chlorination of aromatic hydrocarbons,[2] sulphuric acid or liquid chlorine and the hydrocarbon are introduced through atomisers into a mixing chamber or series of chambers maintained at a suitable temperature, for example, not exceeding 50° C. in the manufacture of benzenemonosulphonic acid, or 30° C. in the manufacture of chlorobenzene, and in the latter case containing a catalyst.[3]

Interesting results have been obtained from the investigation of the effect of catalysts in the continuous sulphonation process of Ambler and Gibbs.[4] The presence of small quantities of the sulphates of a number of metals exerts a slight catalytic action, but the most active catalyst is a mixture of sodium sulphate and vanadium pentoxide in any reasonable proportion, which doubles the amount of benzene sulphonated per minute.[5]

The sulphonation of aromatic compounds may be effected with weaker acid, and in a shorter time, in the presence of a small quantity of iodine.[6] This catalytic action proceeds smoothly when hydroxyl, amino, halogen, or carboxyl groups are present in the molecule, but with difficulty, or not at all, in presence of nitro or sulphonic groups. In certain cases the orientation of the sulphonic group is affected by the catalyst; thus the sulphonation of benzoic acid by this method gives rise to the *o*-sulphonic acid.[7]

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[1] E.P. 147,967; *J.*, 1920, 594A.

[2] H. N. Morris & Co., and H. N. Morris, E.P. 139,234; *J.*, 1920, 291A.

[3] H. N. Morris & Co., and H. N. Morris, E.P. 140,007; *J.*, 1920, 328A.

[4] *Ann. Repts.*, 1919, 4, 88.

[5] J. A. Ambler and W. J. Cotton, *J. Ind. Eng. Chem.*, 1920, **12**, 968; 1920, 743A.

[6] A. Heinemann, E.P. 12,260, 1915; *J.*, 1916, 1008.

[7] J. N. Rây and M. L. Dey, *Chem. Soc. Trans.*, 1920, **117**, 1405; *J.*, 1921, 40A.

A detailed study of the sulphonation of naphthalene has shown that monosulphonation always results in a mixture of the α- and β-isomers, and that even at temperatures below 0° C., at least 2% of the β-acid is formed. It appears that the reaction consists in the formation of a molecular compound which undergoes decomposition into either the α- or β-monosulphonic acid, according to the prevailing external conditions.[8]

The difficulties experienced in the preparation of a chlorobenzene-disulphonic acid were overcome by the discovery that it was produced in quantitative yield by the sulphonation of *p*-chlorobenzenesulphonyl chloride with monohydrate at 160°–180° C.[9]; the product of this reaction is 4-chlorobenzene-1.3-disulphonic acid.[10]

There is some confusion in the literature as to whether the sulphonation product of metanilic acid contains the additional sulphonic group in the 4- or 6- position ; the main product has been shown to be aniline-3.6-disulphonic acid.[11]

Aniline-2.4.6-trisulphonic acid, for which the name trisulphanilic acid is suggested, is obtained in a yield of 30% by heating sulphanilic acid with a mixture of sulphuric acid and phosphoric oxide at 180° C., for eight hours.[12]

Alkali Fusions.

Attention has been directed again to the preparation of phenol from chlorobenzene and aqueous sodium hydroxide under pressure, and the use of a continuous high-pressure autoclave[13] for the process is recommended. It is claimed that this process is more rapid, requires only about 40% of the amount of sodium hydroxide used in the sulphonation and alkaline fusion process, and permits a considerable economy in the amount of acid used.[14]

Aromatic compounds containing a labile halogen atom are heated under pressure with a solution of an alkali hydroxide and a lead salt. The insoluble lead compound formed is filtered and decomposed with acid to liberate the phenol.[15] After the acidification of synthetic sodium phenoxide some 10% of the phenol remains dissolved in the aqueous liquors. A cresylic acid of relatively high boiling point may be used advantageously for the extraction of this phenol, and a recovery of 90–95% of the phenol may be obtained in this manner.[16]

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[8] H. E. Fierz and P. Weissenbach, *Helv. Chim. Acta*, 1920, **3**, 312.

[9] Meister, Lucius, & Brüning, G.P. 260,563 ; *J.*, 1913, 693.

[10] S. C. J. Olivier, *Rec. Trav. Chim.*, 1919, **38**, 356 ; *J.*, 1920, 151A.

[11] S. C. J. Olivier, *Rec. Trav. Chim.*, 1920, **39**, 499.

[12] S. C. J. Olivier, *Rec. Trav. Chim.*, 1920, **39**, 194.

[13] A. M. Aylsworth, E.P. 110,547 ; *J.*, 1918, 229A.

[14] K. Brown, *J. Ind. Eng. Chem.*, 1920, **12**, 279 ; *J.*, 1920, 397A.

[15] E. H. Zollinger and H. Roehling, U.S.P. 1,321,271 ; *J.*, 1920, 9A.

[16] H. M. Dawson, *J.*, 1920, 151T.

Systematic study of the production of resorcinol by the alkaline fusion of sodium benzene-*m*-disulphonate has indicated that 310° C. is the best fusion temperature, two hours the best fusion period, 14–16 mols. of sodium hydroxide to 1 mol. of disulphonate the best fusion mixture, and that the presence of water tends to lower the yield of resorcinol, which, under these conditions, exceeds 60%.[17]

Investigation of the alkaline fusion of *a*-naphthylaminemonosulphonic acids has shown that the reaction product is dependent, in many cases, on the conditions employed, for a highly concentrated alkali leaves an amino group intact, while dilute alkali leads to its replacement by hydroxyl. In no case does the reaction with dilute alkali proceed even approximately quantitatively in any one direction, but several products are always formed. The corresponding aminonaphthol is obtained from all *a*-naphthylaminemonosulphonic acids when highly concentrated potassium hydroxide solutions are employed, whereas dilute solutions exert a powerful oxidising action.[18]

Nitro-compounds.

During the year under review the results of many investigations on nitration and nitro-compounds carried out during the war period have been published. Considerable attention has been directed to a study of the effect on the yield of picric acid of variation of the factors, concentration of sulphuric acid, duration and *temperature of reaction during the preliminary sulphonation of* phenol. The yield of picric acid is proportional to the ratio of di- and monosulphonic acids present in the sulphonation mixture, and is much higher from the disulphonic acid.[19] It is preferable, moreover, to use a sulphonated phenol which contains the maximum quantity of phenol-2.4-disulphonic acid as 2.6-dinitrophenol-4-sulphonic acid is transformed into picric acid more readily than 2.4-dinitrophenol-6-sulphonic acid.[20] The yield of picric acid is increased to 90% when a sulphonation mixture which contains over 80% of phenoltrisulphonic acid is nitrated.[21] Consequently *cæteris paribus*, in the nitration of the phenolsulphonic acids, the yield of picric acid increases in proportion to the amount of polysulphonic acids present in the mixture, for the accumulation of sulphonic groups renders the molecule more resistant to oxidation during nitration.[22] Low yields of picric acid on the large scale have been attributed to the oxidation of phenolsulphonic acids and nitrophenolsulphonic acids, but examination of the technical mother-liquors has shown that an important factor of loss is the presence of dinitrophenolsulphonic acid in these liquors, owing to too short a duration of the reaction at a temperature which has not been sufficiently high.[23]

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[17] M. Phillips and H. D. Gibbs, *J. Ind. Eng. Chem.*, 1920, **12**, 857; *J.*, 1920, 685A.

[18] H. E. Fierz, *Helv. Chim. Acta*, 1920, **3**, 318; *J.*, 1920, 397A.

[19] M. Marqueyrol and P. Carré, *Bull. Soc. Chim.*, 1920, **27**, 195; *J.*, 1920, 350A.

[20] M. Marqueyrol, P. Carré, and P. Loriette, *Bull. Soc. Chim.*, 1920, **27**, 140; *J.*, 1920, 248A.

[21] M. Marqueyrol and P. Carré, *Bull. Soc. Chim.*, 1920, **27**, 199; *J.*, 1920, 350A.

In the oxynitration of benzene with nitric acid in presence of mecuric nitrate, the best yields of nitrophenols are obtained by the use of an excess of benzene. The nitrogen content of the product indicates that it is a mixture of about 52% of dinitrophenol with 48% of picric acid.[24]

The main product of the dinitration of aceto-*m*-toluidide is 4.6-dinitro-aceto-*m*-toluidide, together with a smaller quantity of the 2.6-dinitro derivative, whilst little, if any, of the 2.4-dinitro isomer is formed.[25]

The oxidation of the amino group in 3.4- and 4.5-dinitro-*o*-toluidine with Caro's acid, followed by treatment with nitric acid, affords a convenient method for the preparation of 2.3.4- and 2.4.5-trinitrotoluene, respectively, in good yield,[26] whilst 2.3.6-trinitrotoluene may be obtained in a yield of 50–60% of the 2.6-dinitrotoluene employed.[27]

The nitration of *o*-chlorotoluene with mixed acid produces a mixture of the 3.5-, 5.6-, 4.5-, and 4.6-dinitro-2-chlorotoluenes in a yield of 90%, and the presence of the four isomers shows that the orientation due to methyl is not entirely overpowered by that of the more actively directive chlorine substituent.[28]

The production of picryl chloride from 2.4-dinitrochlorobenzene has been studied with a view to avoiding the use of oleum and excessively high temperature. Conditions have been determined by which a yield of 85% of picryl chloride may be obtained by the use of concentrated sulphuric acid and a reaction temperature of 130° C.[29]

Nitrations which do not proceed readily with nitric acid may be effected by the replacement of sulphonic groups by nitro groups by means of nitrous gases provided that hydroxyl or halogen radicles are also present in the molecule; in the case of sulphonated hydroxycarboxylic acids both the sulphonic and carboxyl groups are replaced by nitro groups.[30]

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[22] M. M. Doll, *Bull. Soc. Chim.*, 1920, **27**, 370; *J.*, 1920, 502A.

[23] M. Marqueyrol and P. Loriette, *Chim. et Ind.*, 1920, **4**, 19T.

[24] L. Vignon, *Bull. Soc. Chim.*, 1920, **27**, 547; *J.*, 1920, 567A.

[25] J. W. Cook and O. L. Brady, *Chem. Soc. Trans.*, 1920, **117**, 750.

[26] O. L. Brady and P. N. Williams, *Chem. Soc. Trans.*, 1920, **117**, 1137; *J.*, 1920, 776A.

[27] O. L. Brady and A. Taylor, *Chem. Soc. Trans.*, 1920, **117**, 876.

[28] G. T. Morgan and H. D. K. Davis, *Chem. Soc. Trans.*, 1920, **117**, 784; *J.*, 1920, 623A.

[29] P. F. Frankland and F. H. Garner, *J.*, 1920, 257T.

The nitration of sulphonated *p*-cymene at 40°–60° C. results in the replacement of the isopropyl group by the nitro group with formation of *p*-nitrotoluene-*o*-sulphonic acid.[31]

In an attempt to determine the position of the two entrant nitro groups in the hexanitrodiphenylamine obtained by the nitration of 2.4.6.3′-tetranitrodiphenylamine, a number of nitro derivatives of diphenylamine have been prepared and examined.[32]

Chlorinated nitronaphthalenes are produced by the action of nitric acid on the chlorine addition products of naphthalene at a low temperature, and heating the products with water or reagents which combine with acids; thus naphthalene dichloride yields 8-chloro-*a*-nitronaphthalene and naphthalene tetrachloride yields 5.8-dichloro-*a*-nitronaphthalene.[33]

The hitherto unknown 1.2.6.8-tetranitronaphthalene and 1.3-dinitroanthraquinone have been isolated and described,[34] and a comparative study of xanthone and anthraquinone has shown that the former is much more reactive than the latter; for instance, whilst only mono- and dinitro derivatives of anthraquinone are known, xanthone yields a number of tri- and tetranitro derivatives.[35]

The mono- and dinitro derivatives of acenaphthenequinone have been described.[36] Mononitroacenaphthenequinone is readily obtained in good yield and may well find technical application; these nitro compounds cannot be prepared by the oxidation of the corresponding derivatives of acenaphthene.[37]

Aromatic Amines.

It appears that the freezing-point is the best criterion of the purity of aniline, and if x represents the percentage of aniline in a sample and t is the observed freezing-point in degrees Centigrade, then $x = 108{\cdot}79 + 1{\cdot}41t$.[38] A detailed study of the preparation of *p*-phenylenediamine[39] and of aniline[40] from *p*-dichlorobenzene

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[30] R. L. Datta and P. S. Varna, *J. Amer. Chem. Soc.*, 1919, **41**, 2039; *J.*, 1920, 172A.

[31] S. V. Hintikka, C.P. 200,291.

[32] C. F. van Duin and B. C. R. van Lennep, *Rec. Trav. Chim.*, 1919, **38**, 358; *J.*, 1920, 151A.

[33] O. Matter, G.P. 317,755; *J.*, 1920, 442A.

[34] S. N. Dhar, *Chem. Soc. Trans.*, 1920, **117**, 1001; *J.*, 1920, 685A.

[35] S. N. Dhar, *Chem. Soc. Trans.*, 1920, **117**, 1053.

[36] F. Mayer and W. Kaufmann, *Ber.*, 1920, **53**, 289.

[37] F. M. Rowe and J. S. H. Davies, *Chem. Soc. Trans.*, 1920, **117**, 1344.

[38] C. L. Knowles, *J. Ind. Eng. Chem.*, 1920, **12**, 881; *J.*, 1920, 717A.

[39] Akt.-Ges. f. Anilinfabr., G.P. 202,170; *J.*, 1908, 1147.

[40] Akt.-Ges. f. Anilinfabr. E.P. 3966, 1908; *J.*, 1908, 1147.

nd monochlorobenzene respectively by the action of ammonia
nder pressure in presence of a catalyst, has shown that positive
esults are obtained only with copper salts. Cuprous salts are more
ctive than cupric and the catalytic action of these salts appears
o be limited to aqueous solution. A yield of 80% of *p*-phenylene-
iamine and 39% of aniline was obtained, although the patent
laims a yield of 80% in the latter case, and no diphenylamine[41]
ould be isolated by the interaction of bromobenzene and aniline
n presence of cuprous iodide.[42]

Attention continues to be directed to the preparation of inter-
nediates from *p*-cymene derived from spruce turpentine, a by-
roduct of the sulphite-cellulose industry, in which it accumulates
t the rate of 1 kg. per ton of cellulose. 3.3′-Dimethyl-6.6′-di-iso-
ropylbenzidine is obtained from crude mononitrocymene by
lkaline reduction to hydrazocymene, which is subjected to the
enzidine transformation.[43] 5-Nitro-2-amino-1-methyl-4-isopropyl-
enzene and 5-amino-2-acetylamino-1-methyl-4-isopropylbenzene,
hich are suitable for use in the manufacture of azo dyes, are
btained from acetylaminocymene in a normal manner,[44] and 2.6-
iamino-1-methyl-4-isopropylbenzene also has been prepared and
sed for making dyes.[45]

o-Nitrophenol-*p*-sulphonyl chloride, 6-nitro-*o*-cresol-*p*-sulphonyl
hloride, and 6-nitrosalicyl-*p*-sulphonyl chloride condense with
mines, diamines, aminocarboxylic acids, aminophenols, etc., in
he benzene and naphthalene series, to form sulphamino com-
ounds, which are reduced to *o*-aminophenol derivatives, preferably
ith sodium sulphide. The products are valuable bases for the
roduction of mordant mono- and disazo dyes, which vary in shade
rom yellow to bluish-violet.[46]

α-Nitronaphthalene-3.6.8-trisulphonic acid in sulphuric acid
olution is readily reduced electrolytically to the corresponding
aphthylamine derivative, but the monosulphonic acids of α-nitro-
aphthalene show a marked difference in their behaviour, for
hilst α-nitronaphthalene-5-(or 8-)monosulphonic acid is reduced
ompletely in acid or neutral solution, α-nitronaphthalene-6-(or 7-)
onosulphonic acid is converted into the corresponding hydroxyl-
mine only, by electrolytic reduction or by reduction with iron
nd ferrous sulphate, and complete reduction to the amine can
nly be achieved in faintly acid solution.[47]

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[41] Akt.-Ges. f. Anilinfabr., F.P. 374,385 ; *J.*, 1907, 756.

[42] A. J. Quick, *J. Amer. Chem. Soc.*, 1920, **42**, 1033 ; *J.*, 1920, 480A.

[43] C. E. Andrews, U.S.P. 1,314,924.

[44] C. E. Andrews, U.S.P. 1,314,923.

[45] J. Alfthan, *Ber.*, 1920, **53**, 78.

[46] H. Bamberger, *Z. angew. Chem.*, 1920, **33**, 8 ; *J.*, 1920, 484A.

[47] H. E. Fierz and P. Weissenbach, *Helv. Chim. Acta*, 1920, **3**, 305 ;
., 1920, 397A.

The preparation of N-methylvinylaniline, $C_6H_5{\cdot}N(CH_3){\cdot}CH:CH_2$, is of interest because it is the first amine to be investigated which contains the vinyl group directly attached to the nitrogen atom. It differs from the known alkylated amines in its instability, for the vinyl group is readily removed in the form of acetaldehyde by hydrolysing agents.[48]

An important reaction of many of the N-substitution products of the arylamines is their rearrangement to C-substitution products. The main product obtained by heating *n*-butylaniline hydrochloride under pressure is 4-amino-*n*-butylbenzene, together with ammonia, aniline, 4-butylamino-*n*-butylbenzene, and smaller amounts of higher butylated products.[49]

The conditions governing the formation of diethylaniline from aniline hydrochloride and ethyl alcohol under pressure in presence of various catalysts have been examined. Sodium bromide, cupric chloride, and calcium chloride jointly function as catalytic agents in this reaction. Calcium chloride and sodium bromide were used originally instead of zinc chloride and potassium iodide respectively on the ground of economy, but actually calcium chloride is much more efficient in alkylation than zinc chloride, whilst potassium iodide is only slightly more efficient than sodium bromide. Consistent yields of 89–91% of diethylaniline were obtained under the best conditions.[50] Alkylaminoanthraquinones are obtained in good yield by the action of a dialkyl sulphate on *α*- and *β*-aminoanthraquinone in presence of a mild alkali and an inert solvent of high boiling point, such as nitrobenzene or tetrachloroethane.[51]

Hydrogenated Naphthalene Derivatives.

The production of hydrogenated naphthalene derivatives by the action of hydrogen on naphthalene in the presence of a catalyst[52] has been successfully established on a technical scale, and the Tetralin G.m.b.H. at the works at Rodleben bei Rosslau are manufacturing large quantities of these products.[53] This fact lends added interest to recent investigations on derivatives of tetrahydronaphthalene, which may prove useful intermediates for dye manufacture. The writer has shown that *α*-naphthylamine is reduced by sodium and an alcohol to 5.8-dihydro-*α*-naphthylamine; the latter, under suitable conditions of temperature and alkali alkyl oxide concentration, undergoes isomerisation to 7.8-(or 5.6-)-dihydro-*α*-naphthylamine, which unlike the 5.8-isomeride is reduced further to ar-tetrahydro-α-naphthylamine.[54] The failure to obtain the tetrahydro compound when alcohols other than amyl alcohol were used, to which reference has been made in a former report,[55] is most probably due to the absence of conditions suitable for this isomerisation. The two dihydro-α-naphthylamines have been isolated and their derivatives described.[56]

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[48] J. von Braun and G. Kirschbaum, *Ber.*, 1919, **52**, 2261.

[49] J. Reilly and W. J. Hickinbottom, *Chem. Soc. Trans.*, 1920, **117**, 103.

[50] T. B. Johnson, A. J. Hill, and J. J. Donleavy, *J. Ind. Eng. Chem.*, 1920, **12**, 636; *J.*, 1920, 594A.

[51] F. W. Atack and W. H. Haworth, E.P. 147,964; *J.*, 1920, 623A.

[52] Tetralin Ges.m.b.H. G.P. 299,012 and 299,013; *J.*, 1920, 743A.

[53] L. Schön, *Oesterr. Chem. Zeit.*, 1920, **23**, 69.

The sulphonation of tetrahydronaphthalene with 100% sulphuric acid results in the formation of the β-monosulphonic acid, which is converted into ar-tetrahydro-β-naphthol by alkali fusion;[57] the α-sulphonic acid of the naphthol is readily obtained and on nitration yields dinitrotetrahydro-β-naphthol. ar-Tetrahydro-β-thionaphthol also has been described.[58]

The hydronaphthalenes are particularly useful solvents; for example, naphthalene crystallised from tetrahydronaphthalene is obtained in an extremely pure condition.[59]

Halogenation.

A study of the kinetics of the chlorination of industrial benzene in presence of iron as a catalyst has shown that the yield of monochlorobenzene increases with the velocity of chlorination but decreases slightly with rise in temperature. The molecular proportion of benzene converted into monochlorobenzene at a particular concentration and in a given time is 8·5 times greater than the molecular proportion of chlorobenzene converted into *p*-dichlorobenzene.[60]

Aluminium is an excellent catalyst for the preparation of chlorobenzene, and 0·1% will produce a steady absorption of chlorine by benzene. In this manner a yield of 87% of monochlorobenzene may be obtained. provided the reaction is stopped when the specific gravity reaches 1·008.[61]

Attention has been directed to *p*-dichlorobenzene with a view to the utilisation of the considerable quantities of this compound which accumulate during the manufacture of monochlorobenzene. *p*-Dichlorobenzene is readily sulphonated to the monosulphonic acid, which is obtained in a yield of 85–90%, and the latter forms 2.5-dichloro-4-nitrobenzenesulphonic acid when nitrated.[62]

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[54] F. M. Rowe, *J.*, 1920, 241T.

[55] *Ann. Repts.*, 1919, **4**, 93.

[56] F. M. Rowe and E. Levin, *Chem. Soc. Trans.*, 1920, **117**, 1574; *J.*, 1921, 41A.

[57] G. Schroeter and W. Schrauth, G.P. 299,603; *J.*, 1919, 893A.

[58] G. Schroeter and W. Schrauth, G.P. 299,604; *J.*, 1920, 398A.

[59] R. Kutschenreuter, G.P. 317,634; *J.*, 1920, 398A.

[60] F. Bourion, *Comptes rend.*, 1920, **170**, 1319; *J.*, 1920, 480A.

[61] J. Meunier, *Comptes rend.*, 1920, **170**, 1451; *J.*, 1920, 526A.

[62] J. H. Crowell and L. C. Raiford, *J. Amer. Chem. Soc.*, 1920, **42**, 145; *J.*, 1920, 397A.

Substitution products which contain chlorine in the side-chain are obtained by the action of hypochlorous acid on an excess of a suitable hydrocarbon at temperatures below 0° C. In the case of toluene, pure benzyl chloride is produced by the fractional distillation of the reaction product, and benzylidine chloride is obtained from benzyl chloride in the same manner. This process is applicable to monochlorotoluenes and the xylenes, but the higher chlorinated toluenes, nitro substitution products, sulphonyl chlorides, and cresol esters do not give side-chain substitution products under these conditions, and sulphonic acids are substituted in the nucleus.[63]

Benzyl chloride, benzyl bromide, and their derivatives may be obtained by the direct introduction of the chloromethyl or bromomethyl group respectively into the aromatic nucleus. An aromatic compound, in presence of a dehydrating agent, is treated with the product obtained by the action of the hydrogen halide on paraformaldehyde or aqueous solutions of formaldehyde, which, in the case of hydrogen chloride, has been shown to consist of *s*-dichloromethyl ether.[64] The sulphonic group is replaced by chlorine, and the chloro derivative obtained in good yield, by passing a current of chlorine into an aqueous solution of a sulphonic acid; sulphonic acids of hydroxy compounds and nitroamines exhibit a special facility for this displacement of the sulphonic group by chlorine.[65] Derivatives of toluene-*p*-sulphonic acid halogenated in the side-chain, are produced by the action of chlorine or bromine on the acid or its dry sodium salt at a high temperature, with or without a halogen carrier. The product consists of the *p*-sulphonic acid of the benzyl or benzylidene halide, according to the quantity of halogen used and the conditions under which the reaction is carried out.[66]

Oxidation.

Considerable attention has been directed to the aerial oxidation of benzene at a high temperature in presence of catalysts. When a mixture of benzene and oxygen or air is passed in the form of vapour over fine pumice impregnated with vanadium oxide at a temperature of 300°–700° C., the reaction product consists of a mixture of quinone, maleic acid, and unaltered benzene together with some by-products. The maleic acid is removed with water, and the residue may be passed a second time over the heated catalyst to increase the quantity of quinone and maleic acid.[67] A benzene solution of quinone submitted to a similar catalytic oxidation in the vapour phase yields maleic acid, and the reaction may be controlled by the use of inert diluent gases.[68] A maximum yield of maleic acid is obtained when equal weights of benzene vapour and air are passed over vanadium oxide at such a velocity that the mixture remains in contact with the catalyst for about ¼ sec. at a temperature of 400°–450° C.[69] The proportions of benzene and oxygen may be varied within wide limits, but as the reaction is probably represented by :—$C_6H_6+7O=(CH)_2(COOH)_2+H\cdot CHO+CO_2$, the optimum quantities will be those indicated by this equation.[70] The plant employed consists essentially of a vaporiser and mixer, a contact tube heated by a metal bath, and a condensing system. The most important factor in the reaction is temperature control when vanadium oxide is used as catalyst for the production of maleic acid.[71] The oxidation of benzene to quinone may also be carried out electrolytically in a vessel containing an electrolyte of greater specific gravity than benzene, so that the latter rises and is oxidised at the anode. The quinone formed dissolves in the excess of benzene, and the process is continued until a sufficient concentration has been obtained. The solution of quinone may be reduced to quinol in a second vessel fitted with an arrangement for bringing the solution in intimate contact with the reducing agent.[72]

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[63] Levinstein, Ltd., H. Levinstein, and W. Bader, E.P. 134,250; *J.*, 1920, 9A.

[64] H. Stephen, W. F. Short, and G. Gladding, *Chem. Soc. Trans.*, 1920, **117**, 510.

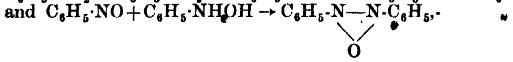
[65] R. L. Datta and H. K. Mitta, *J. Amer. Chem. Soc.*, 1919, **41**, 2028; *J.*, 1920, 172A.

[66] Soc. Chem. Ind. Basle., G.P. 312,959; *J.*, 1920, 398A.

[67] The Barrett Co., U.S.P. 1,318,631; *J.*, 1920, 9A.

The catalytic oxidation of anthracene is effected also by the interaction of oxygen and anthracene vapour at 300°–500° C. in presence of vanadium oxide.[73] According to the interpretation of the oxidation of aniline advanced by Bamberger, phenylhydroxylamine is the initial product of the reaction, but this does not afford a satisfactory explanation of the formation of polynuclear oxidation products. A more reasonable explanation is based on the formation of two different initial products according to the conditions of the reaction. Oxidising agents which readily yield atomic oxygen, such as Caro's acid or hydrogen peroxide, produce the following series of changes :—

$$C_6H_5\cdot NH_2 \rightarrow C_6H_5\cdot NH_2{:}O \rightarrow C_6H_5\cdot NHOH \rightarrow C_6H_5\cdot NO \rightarrow C_6H_5\cdot NO_2$$



$$\text{and } C_6H_5\cdot NO + C_6H_5\cdot NHOH \rightarrow C_6H_5\cdot \underset{\diagdown\,O\,\diagup}{N{-}N}\cdot C_6H_5,$$

whilst under other conditions, the first stage of the reaction consists in the removal of two atoms of hydrogen and further changes are due to the reactivity of the $C_6H_5.N$: residue. This theory is supported by the formation of mixed azo compounds and mixed quinonearyldi-imines by the oxidation of a mixture of two amines.[74]

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[68] The Barrett Co., U.S.P. 1,318,632.

[69] The Barrett Co., U.S.P. 1,314,633 ; *J.*, 1920, 9A.

[70] The Barrett Co., E.P. 122,167 ; *J.*, 1920, 398A.

[71] J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, 1920, **12**, 228 ; *J.*, 1920, 397A.

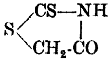
[72] K. & T. Chemical Corp., U.S.P. 1,322,580 ; *J.*, 1920, 100A.

[73] The Barrett Co., U.S.P. 1,355,098 ; *J.*, 1920, 743A.

Under all conditions *p*-nitrotoluene is oxidised to *p*-nitrobenzoic acid most readily by potassium permanganate, the *o*-compound next, and the *m*-isomeride least readily. The conclusion has been drawn that the quantity of nitrotoluene or nitrobenzoic acid entirely destroyed by the oxidising agent is practically constant, and almost independent of the conditions under which the reaction is carried out.[75]

Reference has been made in a former report[76] to the formation of tetrahydroxydianthraquinonyl by the oxidation of alizarin with alkaline hypochlorite. This reaction does not appear to be a general one, but the patent literature indicates that a similar oxidation occurs with erythrohydroxyanthraquinone and quinizarin under somewhat different conditions. Thus, in the alkaline fusion of the former,[77] two molecules condense to form a dihydro compound of the anthrahydroquinone type, which is subsequently oxidised by air to 1.1′-dihydroxy-2.2′-dianthraquinonyl, and further, the reaction mixture obtained by heating quinizarin with salts of weak acids at a temperature slightly above 100° C.[78] consists of 1.4.1′.4′-tetrahydroxy-2.2′-dianthraquinonyl and unaltered quinizarin.[79]

The red dye which Nencki obtained by the oxidation of rhodanine,



with ferric chloride, was manufactured as "Orchil substitute" owing to its fastness to light. This dye was believed to be of an indigoid type, but analysis has shown it to be of a more complex nature than was anticipated. The imino hydrogen of rhodanine does not take part in the oxidation for N-substituted rhodanines are oxidised to similar dyes, but the presence of a free methylene group is essential for dye formation as benzylidene-rhodanine is unaffected by ferric chloride.[80]

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[74] S. Goldschmidt, *Ber.*, 1920, **53**, 28; *J.*, 1920, 224A.

[75] L. A. Bigelow, *J. Amer. Chem. Soc.*, 1919, **41**, 1559; *J.*, 1920, 8A.

[76] *Ann. Repts.*, 1919, **4**, 96.

[77] F. Bayer & Co., G.P. 167,461.

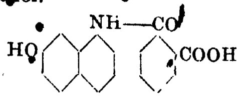
[78] F. Bayer & Co., G.P. 146,223.

[79] R. Scholl, E. Schwinger and O. Dischendorfer, *Ber.*, 1919, **52**, 2254; 1920, 154A.

[80] C. Gränacher, *Helv. Chim. Acta*, 1920, **3**, 152; *J.*, 1920, 225A.

CONDENSATIONS.

A new intermediate for azo dye manufacture, 1-*o*-carboxybenzoylamino-7-naphthol.

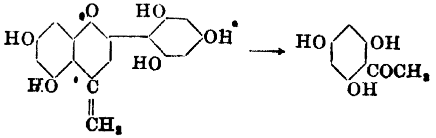


is obtained by the condensation of phthalic anhydride and 1.7-aminonaphthol, followed by alkaline hydrolysis. When unsulphonated *o*-hydroxydiazonium compounds, such as diazotised 4-nitro-*o*-aminophenol, are coupled with this compound, dyes are obtained which produce green shades on wool with chrome mordants.[81]

Phthalic anhydride condenses with phenol in presence of sulphuric acid to form phenolphthalein, but at higher temperatures a mixture of hydroxyanthraquinones is formed, although in poor yield. Contrary to the statements of Friedel and Crafts, phenols condense with phthalic anhydride in presence of aluminium chloride to form hydroxybenzoylbenzoic acids in uniformly good yield, when acetylene tetrachloride is used as solvent. For example, phthalic anhydride and *p*-cresol form 4-hydroxy-*m*-toluoyl-*o*-benzoic acid, $HO.C_6H_3(CH_3)CO.C_6H_4.COOH$, in a yield of 85–90%, and this product is converted into 1-hydroxy-4-methylanthraquinone by treatment with sulphuric acid.[82]

The constitution and conditions of formation of some members of the phthalein and fluoran series have been studied. The condensing agents used, in conjunction with the experimental conditions, influence not only the yield, but also the character of the products formed. The hydroxyl groups of the phthaleins are, as a rule, in the *p*-position, and of the fluorans in the *o*-position with respect to the central carbon atom linking the phthaloyl with the phenolic groups.[83]

Phloracetophenone, an important compound for the synthesis of many natural dyes, has not been directly synthesised hitherto. The product obtained by heating an acetic acid solution of phloroglucinol with zinc chloride is a pyran derivative, produced by the condensation of two molecules of the initially formed phloroacetophenone, from which the latter compound is regenerated by treatment with sodium hydroxide.[84] Thus :—



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[81] F. Bayer & Co., E.P. 145,057.

[82] F. Ullmann and W. Schmidt, *Ber.*, 1919, **52**, 2098 ; *J.*, 1920, **58A**.

[83] M. Copisarow, *Chem. Soc. Trans.*, 1920, **117**, 209 ; *J.*, 1920, **360A**.

[84] K. B. Sen and P. C. Ghosh, *Chem. Soc. Trans.*, 1920, **117**, 61 ; *J.*, 1920, **225A**.

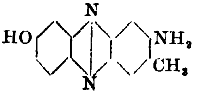
not fast to alkalis or milling owing to the presence of the nitro group.[93]

AZO DYES.

A series of compounds has been prepared in which the anthraquinone nucleus is introduced either into the 1-position of the pyrazolone ring, or as the first component of an azopyrazolone compound, or in both positions together. The colour of the solutions of anthraquinone-azopyrazolones is deep yellow, almost indistinguishable to the eye from those of the benzene-azopyrazolones, as would be expected from Hewitt's theory.[94]

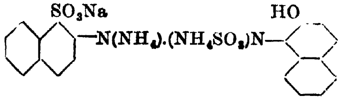
In view of the importance of azo derivatives of pyrazole, it is interesting to note that the dyeing properties of some simple arylazo derivatives of the isomeric glyoxaline have been recorded.[95]

Basic monoazo dyes which produce on tannin-mordanted cotton yellow to red-brown shades, distinguished by their fastness to light, are obtained by coupling the diazonium compound of aminohydroxytoluphenazine :—



with a phenol, a *m*-diamine of the benzene series, or a naphthylaminesulphonic acid such as naphthionic acid.[96]

The ammonium sulphite compound of certain monoazo pigment colours may be salted out from a hot aqueous ammonium sulphite solution; thus, Lithol Red R yields the compound :—



Colour lakes are obtained by heating a solution of these ammonium sulphite compounds with an alkali carbonate in presence of a substratum, such as *blanc fixe.*[97]

An ingenious method for the production of the diazonium derivatives of phenols, cresols, xylenols, and naphthols consists in treating the corresponding sulphonic acid of an aromatic amine with sodium nitrate, whereby sulphurous acid is evolved, with formation of the diazophenol etc.[98] For example, the addition of sodium nitrite to a concentrated aqueous mixture of sulphanilic acid and β-naphthol, with gentle heating, if necessary, results in the rapid formation of *p*-hydroxyphenylazo-β-naphthol.[99]

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[93] P. Demont, *Rev. Gén. Mat. Col.*, 1920, **24**, 64.

[94] K. H. Saunders, *Chem. Soc. Trans.*, 1920, **117**, 1264 ; *J.*, 1920, **777A.**

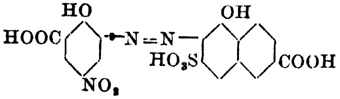
[95] F. L. Pyman, *J. Soc. Dyers & Col.*, 1920, **36**, 107 ; *J.*, 1920, **480A.**

[96] F. à Brassard & Crawford, and A. Singer, E.P. 132,390 ; *J.*, **1919, 894A.**

[97] W. R. Brass, E.P. 134 270 ; *J.*, **1919, 943A.**

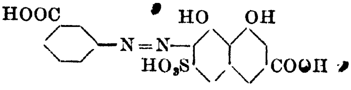
Monoazo dyes are obtained by coupling a diazotised aminophenylsulphonamide with an amine or phenol; dyes of this type are applied in a caustic alkaline solution and fixed on the fibre by precipitation with dilute acid.[100]

Mordant monoazo dyes are produced by coupling *o*-hydroxydiazonium compounds, or preferably their *o*-carboxylic acids, with α-naphthol-3-sulpho-5 (or 6)-carboxylic acid, thus :—



This product dyes wool a red shade which, when after-chromed, is converted into a bordeaux shade fast to fulling and potting, whilst in chrome printing on calico it yields a bordeaux shade fast to soap, chlorine, and light.[101]

Dyes of a similar type are obtained by coupling aromatic diazonium compounds, which do not contain a hydroxyl group in the *o*-position, with 1.8-dihydroxynaphthalenesulphocarboxylic acids: for example, the dye :—



produces a bluish-red shade on wool, which is converted into a fast blue by chroming, whilst the corresponding dye derived from diazotised *p*-aminoacetanilide, printed on calico with a chrome mordant, produces a black shade, fast to light, washing, and chlorine.[102]

Mordant monoazo dyes, which dye wool reddish-blue, blue, or black shades on a chrome mordant, are produced by coupling diazotised *o*-aminophenol-*p*-sulphonic acid, 4-chloro-2-aminophenol-6-sulphonic acid, or 6-nitro-2-aminophenol-4-sulphonic acid with 5.8-dichloro-α-naphthol.[103]

The dyes obtained by coupling diazotised α-naphthylamine,

[98] R. Vidal, F.P. 500,193.

[99] R. Vidal, F.P. 500,192.

[100] J. W. McMyn, E.P. 149,428; *J.*, 1920, 654A.

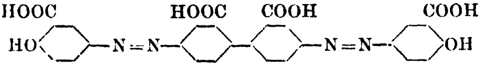
[101] Soc. Chem. Ind. Basle, E.P. 137,733; *J.*, 1920, 262A.

[102] Soc. Chem. Ind. Basle, U.S.P. 1,323,285; *J.*, 1920, 58A.

[103] F. Bayer & Co., E.P. 145,053.

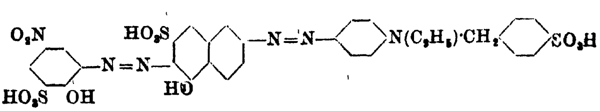
ethoxybenzidine, or *p*-nitraniline, with such oxazines as gallocyanine, Modern Violet, or Phenocyanine, form soluble bisulphite compounds which, when printed on calico with a chrome mordant, *produce moss-green to* marine-blue shades, fast to washing and light.[104]

Yellow to orange monoazo dyes of the general formula $HOOC.R.N{=}N.R(COOH)NH_2$, suitable for wool dyeing or chrome printing on calico, are obtained by coupling diazotised aromatic aminocarboxylic acids with N-methyl-ω-sulphonic acids of the type $R.NH.CH_2.SO_3H$, and subsequent elimination of the N-methyl-ω-sulphonic acid group.[105] When these dyes are diazotised and coupled with an aminonaphtholsulphonic acid, or its acetyl derivative, or a pyrazolone containing a carboxyl group or a carboxyl group and a hydroxyl group in the aryl residue, disazo dyes are formed which produce fast yellow to red or greenish-blue shades on a chrome mordant in wool dyeing or calico printing.[106] Disazo dyes of the type,



when printed on calico with a chrome mordant or a chromium-aluminium mordant, produce yellow shades fast to soap, light, and chlorine. The salicylic acid used for coupling may be replaced by other *o*-hydroxycarboxylic acids such as *o*- or *m*-cresotic acid, or 4-hydroxyisophthalic acid.[107]

Secondary disazo dyes which dye black shades on chrome-mordanted wool are obtained by coupling a diazotised nitroaminophenol or its sulphonic acid with 2.5-aminonaphthol-7-sulphonic acid in alkaline solution, diazotising, and coupling with an alkylaralkylaminesulphonic acid,[108] thus:—



Certain azo dyes may be used for the micro-titration of metals; for example, Diamond Black F forms a deep blue solution with aqueous alkali and various differently coloured lakes are obtained by the addition of ammoniacal solutions of metals. The capacity of a dye to form differently coloured complex compounds soluble in ammonia, is dependent on the presence of a hydroxyl group in the *o*- or *p*-position with respect to the azo group. In acid solution, Diamond Black F is regarded as the quinonoid compound :—

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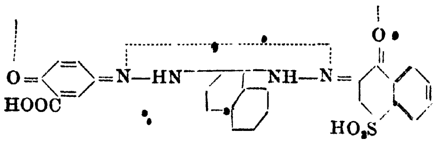
[104] E. Justin-Mueller, *Rev. Gén. Mat. Col.*, 1920, 24, 130; *J.*, 1920, 717A.

[105] Soc. Chem. Ind. Basle, E.P. 141,643; *J.*, 1920, 443A.

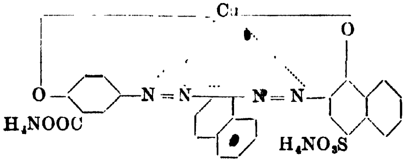
[106] Soc. Chem. Ind. Basle, E.P. 141,401; *J.*, 1920, 443A.

[107] Chem. Works, formerly Sandoz, E.P. 132,995; *J.*, 1920, 329A.

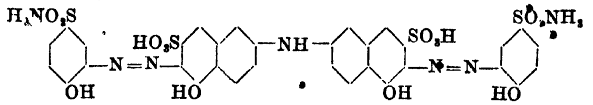
[108] F. Bayer & Co., E.P. 145,056.



in which strong free partial valencies are associated with the *o*- and *p*-oxygen atoms, whilst the other partial valencies of the azo groups satisfy one another. In alkaline solution the former partial valencies are satisfied by the alkali metal and the dye changes to a benzenoid form, whilst the latter partial valencies are satisfied by those of the alkali metal. When, however, the solution contains metallic ions, the subsidiary valencies of which are stronger than those of the alkali metals, the actual metallic lake is formed [109]:—



Secondary disazo dyes are obtained by coupling a suitable derivative of J acid in alkaline solution with two molecules of a diazotised *o*-aminohydroxyarylsulphonamide, *e.g.* :—



These products dye cotton direct in shades sensitive to acids and alkalis, which are converted into violet shades fast to acids, alkalis, and light, however, by coppering.[110]

Disazo dyes suitable for further diazotisation are obtained by coupling a tetrazotised 3.3′-diaminodiarylmethane with two molecules of J acid in alkaline solution.[111]

Trisazo dyes are formed by coupling a suitable 4.4′-diamine of the benzene series with a 1.8-dihydroxynaphthalenesulphonic acid and then with a *m*-diamine; for example, a suitable diamine, obtained by coupling diazotised *p*-nitraniline with 3-amino-4-methoxytoluene and reducing the nitro group, is tetrazotised and coupled with chromotropic acid and *m*-phenylenediamine :—

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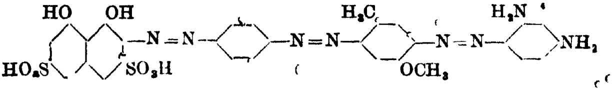
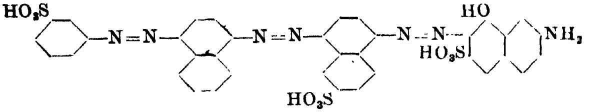
[109] C. Brenner, *Helv. Chim. Acta*, 1920, **3**, 90 ; *J.*, 1920, 250A.
[110] Soc. Chem. Ind. Basle, U.S.P. 1,338,414 ; *J.*, 1920, 443A.
[111] Soc. Chem. Ind. Basle, U.S.P. 1,342,134 ; *J.*, 1920, 512A.



These dyes produce violet shades on cotton, which are converted into black by development with diazotised *p*-nitraniline.[112]

Direct cotton dyes are also obtained by coupling a diazosulphonic acid of the benzene or naphthalene series with a middle component, diazotising and coupling with *a*-naphthylamine, its 6- or 7-monosulphonic acid or a mixture of these acids, diazotising and coupling with 2.8-aminonaphthol-6-sulphonic acid in alkaline solution, *e.g.* :—



These trisazo dyes are diazotised on the fibre and produce grey shades when coupled with *β*-naphthol or *m*-phenylenediamine.[113]

The Diazo Reaction.

The diazotisation of a number of amines has been studied by means of the spectrophotometric method.[114] The reaction is bimolecular, and in the case of aniline its velocity is not modified by doubling the acidity of the solution, whilst the diazotisation of sulphanilic acid is much more rapid when the concentration of the solution is increased, and is favoured by an excess of sodium nitrite.[115]

An interesting application of titanous chloride consists in its use for the production of diazonium compounds; for example, diazobenzene chloride is obtained by the addition of two equivalents of titanous chloride to an aqueous solution of aniline nitrate.[116]

The reversibility of the decomposition of nitrous acid into nitric acid, nitric oxide, and water suggests that solutions of nitrous acid should be stable in presence of nitric oxide under pressure. This principle has been applied to the diazotisation of *m*-dinitroaniline, tribromoaniline, etc., by the condensation of nitrogen trioxide in a cooled tube which contains the amine and hydrochloric acid, after which the tube is sealed and the temperature allowed to rise.[117]

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[112] F. Bayer & Co., E.P. 145,054.

[113] F. Bayer & Co., E.P. 145,055.

[114] E. Tassilly, *Comptes rend.*, 1914, **158**, 489 ; *J.*, 1914, 247.

[115] E. Tassilly, *Bull. Soc. Chim.*, 1920, **27**, 19 ; *J.*, 1920, 184A.

[116] E. Knecht, *J. Soc. Dyers & Col.*, 1920, **36**, 279.

Picramide and other polynitroanilines which are difficult to diazotise owing to their low basicity, are readily diazotised in glacial acetic acid solution by the careful addition in the cold of nitrosylsulphuric acid or sodium nitrite dissolved in monohydrate. The diazotised mixture does not couple when diluted with ice-water, but coupling is effected by the addition of a glacial acetic acid solution of a naphthol at 0° C. As the yields of pure recrystallised azo dyes amount to 80%, it is obvious that diazotisation and coupling must have proceeded smoothly in this process.[118]

CYANINE DYES.

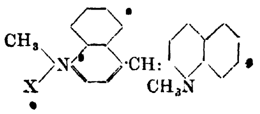
Recent developments in the field of photosensitising dyes have brought lepidine and its derivatives into prominence, and details for the preparation of lepidine, *p*-tolulepidine, and *p*-ethoxylepidine have been published.[119]

The only 2.4-dimethylbenzene-dimethylquinoline hitherto described was incorrectly named[120] and as compounds of this type are of interest in connexion with the preparation of dicyanines, 2.4.6.8-, 2.4.5.7-, and 2.4.5.8-tetramethylquinolines have been synthesised.[121]

The preparation of the nitrate and iodide of Dicyanine A from 2.4-dimethyl-6-ethoxyquinoline has been described.[122]

The introduction of an active auxochrome, such as the dialkylamino group, produces interesting sensitising dyes; the conditions for the preparation of a series of these products by the condensation of the alkyl iodide derivatives of the dialkylaminoquinolines, quinaldines, and lepidines, either with one another or with other bases, have been determined.[123]

The results of experiments on the oxidation of 1.1'-dimethylisocyanine acetate, together with other known facts, have established the following constitution for the isocyanine[124]:—



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[117] E. Briner and R. Jonas, *Helv. Chim. Acta*, 1920, **3**, 366; *J.*, 1920, 399A.

[118] E. Misslin, *Helv. Chim. Acta*, 1920, **3**, 626.

[119] L. A. Mikeska, *J. Amer. Chem. Soc.*, 1920, **42**, 2396.

[120] J. Levin and P. Riehm, *Ber.*, 1886, **19**, 1394.

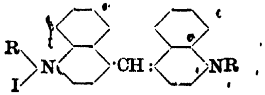
[121] L. A. Mikeska and E. Q. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 2394.

[122] J. A. Mikeska, H. L. Haller, and E. Q. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 2392.

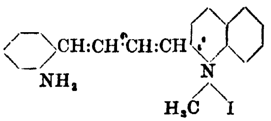
[123] H. Barbier, *Bull. Soc. Chim.*, 1920, **27**, 427; *J.*, 1920, 52[illegible]A.

[124] W. H. Mills and R. S. Wishart, *Chem. Soc. Trans.*, 1920, **117**, 579; *J.*, 1920, 540A.

which is confirmed by the formation of isocyanines from lepidine.[125] This practically fixes the constitution of cyanines as :—



In certain respects *o*-aminocinnamylidenequinaldine methiodide :—



bears a distinct relationship to the dyes of the cyanine class, yet it has no action on a gelatinobromide photographic plate, although it dyes wool and silk a rich reddish-brown shade, very fugitive to light.[126]

ANTHRAQUINONE DYES.

Anthranol is obtained by heating anthraquinone with glucose and a 30% solution of sodium hydroxide in an autoclave at 230° C. for 5–10 hours.[127]

Examination of the behaviour of *a*- and *β*-hydroxyanthraquinones, Purpurin, Alizarin Bordeaux, and hydroxyanthrapurpurin has shown that hydroxyl groups in the *β*-position are more readily acetylated than those in the *a*-position.[128]

The orientation of the sulphonic groups in Alizarin Irisole (a monosulphonic acid of mono-*p*-toluidinoquinizarin) and Alizarin Cyanine Green G (a disulphonic acid of di-*p*-toluidinoquinizarin) has been determined by the isolation of leucoquinizarin and *p*-toluidine-3-sulphonic acid as the reduction products of these dyes with hydriodic acid. These dyes, which are prepared by sulphonation, are, therefore, isomeric with Alizarin Direct Violet R and Alizarin Direct Green G, which are obtained by the condensation of quinizarin or leucoquinizarin with one or two molecules of *p*-toluidine-2-sulphonic acid respectively. It is interesting to note a striking difference between *p*-toluidine-2-sulphonic acid and *p*-toluidine-3-sulphonic acid, for whilst the former readily condenses with quinizarin or leucoquinizarin, the latter, probably as a result of internal salt formation, does not condense.[129]

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[125] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2389.

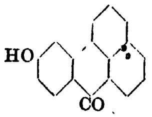
[126] W. H. Mills and P. E. Evans, *Chem. Soc. Trans.*, 1920, **117**, 1035; *J.*, 1920, 685A.

[127] A. G. Perkin, E.P. 151,707; *J.*, 1920, 743A.

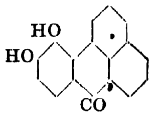
[128] O. Dimroth, O. Friedemann, and H. Kämmerer, *Ber.*, 1920, **53**, 481; *J.*, 1920, 399A.

[129] R. Meyer, *Ber.*, 1920, **53**, 1265; *J.*, 1920, 567A.

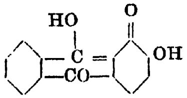
The *o*-dihydroxybenzanthrone derived from deoxyalizarin (the anthranol corresponding to alizarin), for which the name benzalizarin has been proposed, resembles alizarin in many of its properties, for it dyes mordanted wool in shades which, with the exception of that given by iron, are identical with those produced by the latter, although of a slightly more orange tint. In all probability the mono- and dihydroxybenzanthrones have the constitution :—



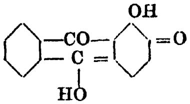
and



The fact that the dyeing properties of benzalizarin so closely resemble those of alizarin is of interest, for those of the latter have been assumed to be due to the presence of two hydroxyl groups in the *o*-position with respect to one another, one of which is adjacent to a carbonyl group. Based on this view, an *o*-quinonoid structure (I) has been proposed for the alizarin lakes, but if the constitution attributed to benzalizarin is correct, a *p*-quinonoid form (II) would prove more applicable[130] :—



(I)



(II)

Anthraquinone Vat Dyes.

The condensation product obtained by boiling 1-acetylamino-anthraquinone with phosphorus oxychloride, when treated with sulphuric acid, produces a red powder which dyes cotton in red-brown shades from a brown vat.[131]

A detailed study of 1-hydroxy-4-chloroanthraquinone and some of its derivatives has shown that only chlorine atoms which are in the *a*-position in hydroxychloroanthraquinones are replaced by hydroxyl by treatment with boric and sulphuric acids at 156°–160° C.

Anthraquinone-acridone is obtained by the action of sulphuric acid on anthraquinonyl-anthranilic acid, but in the case of N(1-hydroxyanthraquinonyl-4)-anthranilic acid, the action of acetic anhydride in presence of pyridine, and subsequent treatment of the acetyl derivative with *p*-toluenesulphonyl chloride is necessary in order to obtain 4-hydroxyanthraquinone-2.1-acridone :—

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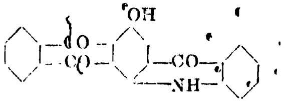
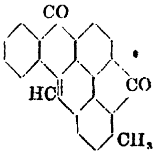
[130] A. G. Perkin, *Chem. Soc. Trans.*, 1920, **117**, 696 ; *J.*, 1920, 623A.

[131] B. A. S. F., E.P. 10,291, 1913 ; *J.*, 1914, 544.



This compound dyes blue shades on cotton from a wine-red vat, and consequently the hydroxyl group in the *p*-position exerts the same influence on the shade as an amino group in that position.[132]

1-Methylphenanthro-anthraquinone-fluorenone :—



is of interest on account of the combination of the anthraquinone complex with the intensely orange-red coloured phenanthraquinone, yet, although it forms a brown vat-like solution with alkaline hydrosulphite, it has no affinity for vegetable fibres.[133]

INDIGOID VAT DYES.

Oxidation in cold sulphuric acid suspension with a current of chlorine in presence of a concentrated aqueous solution of a sodium halide affords a ready method for the conversion of indigo or its homologues into halogenated isatins; for example, mono- or dibromo-isatin is obtained when two or four molecules of sodium bromide respectively are employed.[135]

A greenish-blue vat dye for wool or cotton is produced by the action of acetaldehyde or paraldehyde on a sulphuric acid solution of indigo at a low temperature.[136]

Baeyer and Drewson's synthesis of indigotin by the action of dilute sodium hydroxide on an acetone solution of *o*-nitrobenzaldehyde has been extended to the preparation of 6.6′-dicyano-indigotin from 2-nitro-4-cyanobenzaldehyde. This new derivative of indigotin dyes cotton or wool from the vat in reddish-purple shades which are oxidised to a fine blue, tinged with violet, on exposure to air, although the oxidation proceeds more slowly than is the case with indigotin.[136]

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[132] F. Ullmann and A. Conzetti, *Ber.*, 1920, **53**, 826 ; *J.*, 1920, 480A.

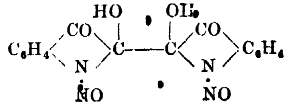
[133] A. Schaarschmidt and J. Herzenberg, *Ber.*, 1920, **53**, 1807.

[134] Soc. Chim. Usines du Rhône, F.P. 490,281.

[135] Konsortium f. Elektrochem. Ind, G.P. 310,197 ; *J.*, 1920, **399A**.

[136] S. Reich and E. Lenz, *Helv. Chim. Acta*, 1920, **3**, 144 ; *J.*, 1920, 224A.

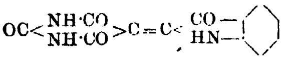
In order to investigate the course of the degradation by which benzoylformic acid ethyl ester is obtained by the action of nitrous gases on indigotin in presence of ethyl alcohol, ether has been substituted for the alcohol, and a product isolated in good yield which is believed to be dinitrosodihydroxy-(dihydroindigo) :—



This compound is partially converted into a substance, believed to be nitrosohydroxy-(dihydroindigo), together with isatin and benzoylformic acid ester, when it is gently warmed with alcohol.[137]

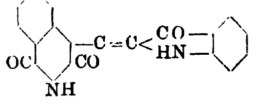
The reduction products of the azo derivatives, which are readily obtained by coupling diazonium compounds with indoxyl, are, in the case of benzene-azo-indoxyl, aniline, ammonia, and indirubin.[138]

The addition of some of the technical melt of indoxyl to a hot acetic acid solution of alloxan produces 5-(dioxy-2.4-pyrimidine)-2-indole-indigo :—



which dyes wool and silk in heliotrope shades, whilst its sulphonic acid dyes violet shades.[139]

o-Homophthalimide (1.3-dioxyisoquinoline) readily condenses with *a*-isatin-anilide to form 1-oxy-4-isoquinoline-2′-indole-indigo :—



which is decomposed by dilute alkalis, but forms a colourless vat with zinc and acetic acid, from which wool is dyed in fine dark violet shades. The isomeric compound from *β*-isatin-anilide is rather more stable to alkalis but possesses no dyeing properties, whilst 1-oxy-4-isoquinoline-2-thionaphthene-indigo, although readily vatted, has little affinity for the fibre.[140]

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[137] T. Posner and G. Aschermann, *Ber.*, 1920, **53**, 1925.

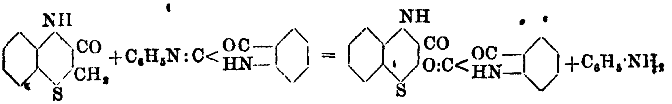
[138] J. Martinet and O. Dornier, *Comptes rend.*, 1920, **170**, 592; *J.*, 1920, 292A.

[139] J. Martinet and O. Dornier, *Comptes rend.*, 1920, **171**, 184; *J.*, 1920, 594A.

[140] W. Herzog, *Ber.*, 1920, **53**, 564; *J.*, 1920, 399A.

The oxidation of indoxyl and α-naphthol in acid solution with ferric chloride produces a mixture of 2-naphthalene-2-indole-indigo and 4-naphthalene-2-indole-indolignone, whilst oxidation of the indoxylcarboxylic acid melt and α-anthranol by this method yields 2-anthracene-2-indole-indigo, identical with the dye obtained from α-isatin-anilide and α-anthranol.[141] In a similar manner, 2-thionaphthene-2'-indole-indigo may be prepared from indoxylic acid and 3-hydroxy-1-thionaphthene.[142]

Benzoketodihydrothiazine and α-isatin-anilide react in a high-boiling solvent, such as ethyl benzoate, thus:—



to form 2-(benzodihydro-1.4-thiazine)-2-(indole)-indigo, which dyes cotton in bluish-violet shades, and wool, for which it exhibits a somewhat greater affinity, in reddish-violet shades, from a greenish-yellow vat. The products obtained from benzoketodihydrothiazine and thionaphthenequinone-anilide or β-isatin-anilide in a similar manner, possess little affinity for textile fibres. The inferior dyeing properties of these compounds compared with those of indigo or Thioindigo Red are in agreement with the hypothesis of Claas,[143] as the former contain only one quinonoid indogen whilst the latter contain two such groups.[144]

The isolation of thionaphthene from crude naphthalene by means of sodamide at 120° C., and treatment of the sodium compound with water, has been described. Sodium thionaphthene is a mixture of two parts of the monosodium with one part of the di-sodium compound, and is converted by carbon dioxide in presence of an inert solvent into a mixture of thionaphthene-2-carboxylic acid and thionaphthene-2.3-dicarboxylic acid. The latter is converted into the imide, from which 3-hydroxythionaphthene is obtained, which yields Thioindigo Red on oxidation.[145]

SULPHIDE DYES.

The use of aloe resin and aloes in the sulphide fusion has been described[146] and a sulphide dye has also been obtained by the replacement of the calcium in sulphite-cellulose waste liquors by another non-alkaline base, and heating the product with polysulphides.[147]

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[141] A. Jolles, G.P. 305,558 ; *J.*, 1919, 894A.

[142] A. Jolles, G.P. 305,559 ; *J.*, 1920, 718A.

[143] *J.*, 1916, 1150.

[144] W. Herzog, *Ber.*, 1910, **52**, 2270 ; *J.*, 1920, 152A.

[145] R. Weissgerber and O. Kruber, *Ber.*, 1920, **53**, 1551 ; *J.*, 1920, 716A.

[146] The Import & By-Products Co., U.S.P. 1,346,153 and 1,346,154 ; *J.*, 1920, 594A.

A variation of the well-known method for the production of a sulphide black by boiling 2.4-dinitrophenol with aqueous polysulphide under a reflux condenser, consists in the addition of commercial cresol or phenol to the mixture. The product dyes cotton a direct black, which does not bronze, is without greyish reflection, and is fast to chlorine.[148]

Blue and black sulphide dyes are produced by the action of sulphur on the mixture obtained when an aromatic amine and a nitrocresol, nitrophenol, or nitronaphthol, are treated with one-half the quantity of alkali sulphide necessary to reduce the nitro compound to the corresponding amine.[149]

The fact that yellow sulphide dyes are obtained from the sulphur fusion of *m*-toluylenediamine or acyl derivatives of *m*-phenylenediamine, but not from *m*-phenylenediamine, has led to the assumption that these dyes contain thiazole rings, and moreover, the presence of a considerable number of free amino groups was to be expected, but actually the reaction with nitrous acid is inappreciable. Examination of the yellow dye formed by the fusion of diformyl-*m*-toluylenediamine with sulphur has shown that it contains no oxygen, and that the proportion of carbon to nitrogen is less than in diformyl-*m*-toluylenediamine, but greater than in *m*-toluylenediamine. On account of the tendency of sulphur to form polysulphide chains with any number of sulphur atoms, a formula such as $(C_{17}H_{14}N_4S_{6\cdot27})_n$ probably expresses the composition of this dye more correctly than one containing an integral number of sulphur atoms, but agreeing less closely with the analytical results. Oxidation in alkaline solution with permanganate gives rise to a product believed to be formed thus:—

$$(C_{17}H_{12}N_4S_2)_6(S.SH)_5(S.S.SH)_5 \longrightarrow (C_{17}H_{12}N_4S_2)_6(SO_3H)_{10}$$

Consequently the dye complex formed from twelve molecules of diformyl-*m*-toluylenediamine would contain five ·S·SH groups and five ·S·S·SH groups, and as twelve sulphur atoms only remain for ring formation, only half the nitrogen can be involved in thiazole rings.[150]

SELENIUM DYE.

The preparation of 3.6-tetramethyldiaminoselenopyronine by the interaction of tetramethyldiaminodiphenylmethane, sodium selenite, and fuming sulphuric acid, and its isolation as the crystalline zincichloride, $C_{17}H_{19}N_2SeCl_2,ZnCl_2$, has been described.[151]

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[147] J. S. Robeson, U.S.P. 1,316,742; *J.*, 1919, 894A.

[148] H. R. Vidal, E.P. 141,759; *J.*, 1920, 443A.

[149] R. Vidal, F.P. 500,193.

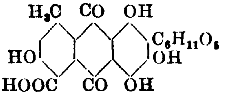
[150] J. K. Mazumda and E. R. Watson, *Chem. Soc. Trans.*, 1920, **117**, 830; *J.*, 1920, 624A.

Natural Dyes.

The successful revival of the indigo industry in India would now appear to be assured. The formation of the Indigo Planters' Coöperative Association was undoubtedly a step in the right direction which has been long overdue, and as it is hoped that sulphuric acid will soon be available in large quantities in India, the difficulty with regard to the necessary supply of phosphatic manures will, no doubt, be overcome.[152]

The preparation of hæmatoxylin by the extraction of logwood extract with ether, followed by crystallisation from water, has been described.[153]

The close resemblance of the absorption spectra and dyeing properties of carminic acid and kermes dye suggests that the former is, like the latter, a hydroxyanthrapurpurin derivative. This is actually the case, and the side-chain, considered to be $C_6H_{11}O_5$, contains four hydroxyl groups and possibly possesses a structure of the type of sugar, although carminic acid is not a glucoside. It must contain at least one asymmetrical carbon atom for carminic acid and its derivatives, unlike kermesic and laccaic acids, are optically active. The structure of carminic acid, so far as it has been elucidated at present,[154] is :—



Rubiadin monomethyl ether (the methyl ether of 1.3-dihydroxy-4-methylanthraquinone) and alizarin-*a*-methyl ether have been isolated from the residue obtained after the extraction of morindin from *Morinda citrifolia*. Rubiadin monomethyl ether is identical with the substance obtained from *Morinda longiflora* and erroneously described [155] as 1.3-hydroxymethoxy-2-methylanthraquinone.[156] A slight modification of Perkin and Yositake's chroman formula for catechin has been proposed,[157] viz. :—

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[151] M. Battegay and G. Hugel, *Bull. Soc. Chim.*, 1920, **27**, 557 ; *J.*, 1920, 567A.

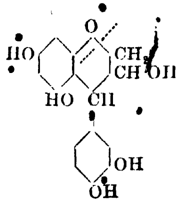
[152] H. E. Armstrong, *The Times*, April 8th, 1920 ; *J.*, 1920, 131R.

[153] P. A. Houseman and C. K. Swift, *J. Ind. Eng. Chem.*, 1920, **12**, 173 ; *J.*, 1920, 329A.

[154] O. Dimroth and H. Kämmerer, *Ber.*, 1920, **53**, 471 ; *J.*, 1920, 399A.

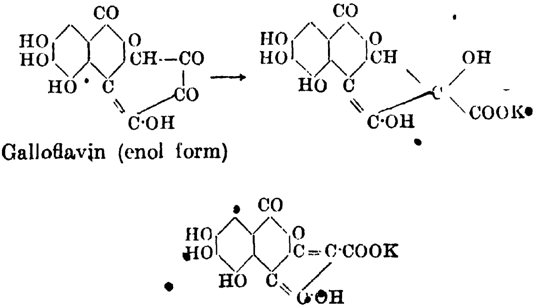
[155] M. Barrowcliff and F. Tutin, *Chem. Soc. Trans.*, 1907, **91**, 1907 ; , 1907, 1273.

[156] J. L. Simonsen, *Chem. Soc. Trans.*, 1920, **117**, 561 ; *J.*, 1920, 540A.



The methylated reduction product of catechin tetramethyl ether, which has been variously regarded as 2.4.6.3′.4′-pentamethoxy-3-ethyldiphenylmethane and as 2.4.6.3′.4′-pentamethoxy-αγ-diphenylpropane, has been shown to be 3.4.2′.4′.6′-pentamethoxy-αα-diphenylpropane.[158]

Further investigation of galloflavin, which is obtained by the oxidation of alkaline solutions of gallic acid with air, has led to interesting results. Galloflavin contains four hydroxyl groups and forms a tetramethoxy derivative, one methoxy group of which is readily hydrolysed by alkali with simultaneous isomerisation and formation of trimethoxyisogalloflavin.[159] The degradation of the latter compound to 3.4.5-trimethoxyphthalide, in conjunction with other facts, points to the following constitution for these compounds, which are related according to the scheme[160] :—



Galloflavin (enol form)

Isogalloflavin (enol form)

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[157] M. Nierenstein, *Chem. Soc. Trans.*, 1920, **117**, 971 ; *J.*, 1920, 685A.

[158] M. Nierenstein, *Chem. Soc. Trans.*, 1920, **117**, 1151 ; *J.*, 1920, 777A.

[159] J. Herzig and R. Wachsler, *Monatsh. Chem.*, 1914, **35**, 75; *J.*, 1914, 130.

[160] J. Herzig, *Annalen*, 1920, **421**, 247.

The colouring matter of the red pea gall, for which the name dryophantin is proposed, has the empirical formula $C_{23}H_{28}O_{15}$, and on hydrolysis with sulphuric acid yields dextrose and purpurogallin, thus:—

$$C_{23}H_{28}O_{15}+2H_2O=2C_6H_{12}O_6+C_{11}H_8O_5$$

This colouring matter, therefore, is not an anthocyanin, and as the other so-called anthocyanins of plant galls are probably of the same nature, it is proposed to classify these red pigments in a new group, to which the name gallorubrones is assigned.[161]

[161] M. Nierenstein, *Chem. Soc. Trans.*, 1919, **115**, 1328; *J.*, 1920, 107A.

FIBRES, TEXTILES, CELLULOSE, AND PAPER.

By Sidney S Napper, F.I.C., A.C.G.I.

There is a notable improvement in the quality and quantity of the work being done on cellulose and its derivatives; interest in the subject is increasing to such an extent that it has been proposed to form a Cellulose Section of the American Chemical Society. Textile fibres have not shared in this revival, and it is doubtful whether the Research Associations which have been formed in the silk, linen, woollen, and cotton industries will consent to any considerable extent to the publication of work done in their laboratories.

This section is pre-eminently dependent on the development of economic botany, as even in the case of silk and wool the actual producer has to rely on vegetable raw materials, and the experience of the writer in preparing this report impels him to endorse C. F. Cross's appeal for more widespread study of this subject, which has met with strong support from Prof. J. B. Farmer.[1] It is to be hoped that the offer of a Research Fellowship and Prize by Sir Thomas Latham and Messrs. Cross and Bevan under the auspices of the Society of Chemical Industry, will meet with the response that is due to the importance of the subject and the public spirit and generosity of the donors

Fibres and Textiles.

Cotton.

A paper by E. Knecht and F. V. Fernandes[2] contains some interesting information regarding the purification of raw cotton by extracting it with various solvents. In experiments previously recorded the extracts were evaporated to dryness on a water-bath, and the results obtained in this way were found to be lower by 10–20% than when the evaporation and drying were carried out in a vacuum desiccator. The authors express some doubt as to whether the latter method is efficient, but as the amount of water taken up on exposure to the air is about the same in both cases it appears that in the earlier experiments there was some decomposition or volatilisation. The purification of the cotton did not affect the affinity of the fibre for methylene blue, although the absorption of tannic acid was reduced by half and the extracts contained substances which precipitated tannic acid from aqueous solution. The figures for continued extraction with alcohol and with water showed a gradual loss, which may have been due to decomposition of the material.

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[1] *J.*, 1920, 157R.

[2] *J. Soc. Dyers and Col.*, 1920, **36**, 43; *J.*, 1920, 481A.

E. Knecht has also published[3] a preliminary notice of work on the prolonged action of moderate heat on cotton and other cellulose and textile materials. The results, which are of a qualitative nature, show that a temperature of 93° C. causes considerable decomposition in the course of periods amounting to several hundred hours. W. A. Lawrance[4] gives figures showing the loss of strength of cotton yarn when treated with dilute sulphuric acid solutions and dried at different temperatures, and discusses the bearing of the results on the carbonising process. N. Fleming and A. C. Thaysen[5] describe observations on the bacterial deterioration of damp cotton during storage. They find that this action ceases when the proportion of moisture falls to less than 9%.

Wool.

There has not been much advance in our knowledge of the nature and properties of wool since the last report. J. I. Hardy[6] discusses the influence of the diameter and humidity on the tensile strength and elasticity of scoured and unscoured wool, and P. Krais and P. Waentig[7] give their views as to the nature of, and conditions favourable to the development of Allwörden's reaction. They point out that, at the boiling-point, traces of alkali dissolved from the glass vessel employed may be sufficient to inhibit the reaction.

Some attention is being paid to the scouring process. H. Hey[8] discusses in considerable detail the application of volatile solvents to the degreasing of wool and textiles. T. Hollis and A. Woodmansey[9] claim a process for scouring at the ordinary temperature in open machines with various oils and oily mixtures; and H. Y. McBride[10] in cleaning dry wool employs dry pulverised cleaning and lubricating materials in the combing process, the material moving in counter-current to the fibre.

The favourable influence of nitrogenous colloids in liquors employed for the treatment of wool[11] has been investigated by

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[3] *J. Soc. Dyers and Col.*, 1920, **36**, 195; *J.*, 1920, 640A.

[4] *Canad. Chem. J.*, 1919, **3**, 329; *J.*, 1919, 894A.

[5] *Biochem. J.*, 1920, **14**, 25; *J.*, 1920, 263A.

[6] *J. Agric. Res.*, 1920, **19**, 55; *J.*, 1920, 481A.

[7] *Neue Faserstoffe*, 1919, **1**, 265; *J.*, 1920, 329A.

[8] *J. Soc. Dyers and Col.*, 1920, **36**, 11; *J.*, 1920, 185A.

[9] E.P. 137,747; *J.*, 1920, 360A.

[10] U.S.P. 1,323,641; *J.*, 1920, 59A.

[11] *Ann. Repts.*, 1919, **4**, 116.

L. Rinoldi[12] who finds that improved results follow from the use of 2–3 parts of glue for every 1–2 parts of soap in the scouring bath.

The views on the resistance of wool to weather put forward by A. Kertesz last year have not been accepted without discussion; in a later paper[13] he writes in support of the view that a chrome treatment improves the resistance of the material, and criticises the value of the results of Von Kapff[14] who maintains the opposite opinion. A. Grass[15] points out that the results of both these workers are based on conditions which are either abnormal or out of harmony with industrial practice.

Another preservative process is proposed by L. Cassella und Co.,[16] who recommend the use of tannin and suggest that the biuret test should be employed in arriving at the optimum conditions of treatment. K. Wagner[17] describes a case in which wool that had been exposed to atmospheric action gave unsatisfactory results on re-dyeing, apparently due to the degradation of the proteid molecule. The best results were obtained by dyeing in an acid bath but even then the material dyed irregularly.

Silk.

The contributions to this section are few in number and of a doubtful value which time must be left to settle. The question of the boiling-off process for the removal of silk gum is still receiving attention and F. Bayer und Co.[18] claim to have established conditions under which silk may be satisfactorily degummed by means of dilute alkaline solutions under pressure. The use of either sodium hydroxide, carbonate, phosphate, or borate is suggested. A final review of the subject is not possible pending the publication of the work which has been carried out under the direction of S. B. Schryver for the Silk Association.

J. Korselt has made further additions to processes for the treatment of silk; in one patent[19] he suggests the use of a 0·1–2·0% solution of catalase for about 30 min. at 40° C., with or without creatinine, and in another patent[20] claims the use of certain nitrogen derivatives for treating loaded silk and makes the rather surprising claim that the yarn "immediately" increases in strength by 50–60%.

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[12] *Prog. Ind. Tint. Tess.*, 1920, **19**, 18.

[13] *Färber-Zeit.*, 1920, **31**, 1; *J.*, 1920, 481A.

[14] *Färber-Zeit.*, 1919, **30**, 23.

[15] *Färber-Zeit.*, 1920, **31**, 64; *J.*, 1920, 481A.

[16] G.P. 303,223; *J.*, 1920, 228A.

[17] *Färber-Zeit.*, 1920, **31**, 52; *J.*, 1920, 512A.

[18] G.P. 301,255; *J.*, 1920, 13A.

[19] E.P. 108,489; *J.*, 1920, 482A.

[20] E.P. 136,578; *J.*, 1920, 186A; *cf.* *Ann. Repts.*, 1918, **3**, 124.

M. Battegay and T. Voltz[21] discuss the colour reactions and the solubility of silk in ammoniacal nickel solution, which by analogy with the biuret reaction, they consider are due to the formation of some complex metallic salt with a cyclic structure.

Flax, Hemp, etc.

Rossi's process of retting with a culture of *B. Comesii* has been reported on favourably by the Canadian Department of Trade and Commerce,[22] which considers it superior to and cheaper than the ordinary method. D. Carbone[23] gives further information regarding the retting of hemp with *B. felsineus*, the agent employed in his process, which differs considerably from that of Rossi.[24] P. Krais[25] describes the results of further experiments on the retting process in presence of sodium bicarbonate, the action being largely due to *Plectridiæ*,[26] and the effects observed after adding sodium sulphite and glucose to the liquor. W. J. Robinson[27] claims a process for drying at 43°–55° after treating flax and hemp with a soap solution containing turpentine, and P. Püschel[28] one for washing with water at 30° C. after retting, and then passing through squeezing rollers before artificial drying. In connexion with these last processes it is interesting to note that the Verband deutscher Leinen-Industrieller has offered a prize of 10,000 marks for a practical method which will permit retted flax and hemp to be dried artificially without any loss of quality.

R. Haller[29] describes the behaviour of flax and hemp fibres on treatment with concentrated caustic soda solution. This affords a means of distinguishing between the materials which behave in an entirely different manner towards this reagent; flax, for instance increases in diameter by about 83%, while hemp shows an increase of only 25%. Numerous other points of difference are described.

Y. Uyeda[30] gives the results of analysis of Korean hemp and ramie, and discusses their application for textile purposes.

	Hemp. %	Ramie. %
Moisture	8·83	10·50
Soluble in water	4·50	3·79
„ „ 1% NaOH	18·53	17·27
Cellulose	62·42	65·88
Lignin	3·32	0·66

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[21] *Bull. Soc. Chim.*, 1920, **27**, 536; *J.*, 1920, 568A.

[22] *Weekly Bull.*, 1919, 1185.

[23] *Bull. Agric. Intell.*, 1919, **10**, 477; *J.*, 1920, 443A.

[24] *Ann. Repts.*, 1918, **3**, 119.

[25] *Z. angew. Chem.*, 1919, **32**, 326; *J.*, 1920, 11A.

[26] *Z. angew. Chem.*, 1920, **33**, 102; *J.*, 1920, 443A.

[27] E.P. 141,982; *J.*, 1920, 444A.

[28] G.P. 305,682; *J.*, 1920, 13A.

[29] *Neue Faserstoffe*, 1919, **1**, 229; *J.*, 1920, 292A.

[30] *J. Ind. Eng. Chem.*, 1920, **12**, 573; *J.*, 1920, 541A.

J. Read and H. G. Smith [31] describe very fully the nature of the crude fibre from *Posidonia australis*, its treatment and suitability for textile purposes, and the properties of the cellulose obtained by chemical treatment. It appears to be a definite lignocellulose intermediate between jute and wood, and yields a cellulose very similar to that given by esparto.

As a result of the shortage of textile materials in Germany a large number of proposals have been made for dealing with all classes of vegetable matter; among reagents and processes for the general treatment of vegetable materials are the use of soap-makers waste lye, oxidising agents, weakly acid magnesium sulphite, vegetable enzymes (such as potato juice), malt and fermentation, and superheated steam followed by sudden cooling; whilst among the substances to be treated by special processes for the production of textile fibres are hop bark, hop bines, willow or poplar bark, lupin stems, reeds, rushes, pea-pods, typha, straw, mallows, and yucca.

The further treatment of some of these vegetable fibres to render them more suitable for spinning, and to give them a physical character more nearly resembling those of the commonly employed textile fibres, is receiving increasing attention. The subject of "cottonising" vegetable fibres is treated in its general aspects by E. O. Rasser [32]; detailed processes are described in the case of broom fibres by the Nessel-Anbau Ges. m. b. H.,[33] and mulberry bark by G. Mark,[34] both of whom employ strongly alkaline substances.

For obtaining a "wool effect" on vegetable fibres Gillet et Fils and C. Schwartz [35] treat them with a solution containing 3–9% of cellulosic material in nitric acid of about 65–70% strength. They claim that a coating of nitrated cellulose is produced; it is possible that in addition the acid has a mercerising effect. They also suggest [36] the use of starch dissolved in nitric acid for the same purpose. In a further patent [37] they suggest that washing the treated fibre with solutions of acids, bases, or salts, instead of pure water, results in a more rapid and complete precipitation of the nitrated cellulose.

P. Krais and O. Röhm [38] claim that a permanent silky gloss can be produced on flax, hemp, etc., by treatment with pancreatic enzymes; and M. Böhm und Sohn[39] assert that stiff, smooth fibres such as kapok, asclepia, and typha may be rendered soft and pliable by treatment with dilute solutions of pyridine bases.

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[31] *Comm. of Australia, Inst. Sci. and Ind. Bull. No.* 14, 1919; *J.*, 1920, 11A.

[32] *Monatschr. Textilind.*, 1919, **34**, 41; *J.*, 1920, 11A.

[33] G.P. 315,754; *J.*, 1920, 330A.

[34] G.P. 317,043; *J.*, 1920, 360A.

[35] E.P. 136,568; *J.*, 1920, 513A.

[36] E.P. 144,204; *J.*, 1920, 542A.

[37] E.P. 144,563; *J.*, 1920, 541A.

[38] G.P. 315,398; *J.*, 1920, 292A.

Artificial Silk.

The properties of artificial silk and other new fibres have been investigated by P. Krais[40] particularly with reference to their behaviour on wetting. The swelling and loss of strength are described, and the effect of chemical after-treatment is considered. Artificial silk increases in diameter by 45% on wetting and nettle fibre by 11%.

Z. Ostenberg[41] proposes to spin a solution of a vegetable proteid material such as gliadin or zein containing a small proportion of a toughening and softening agent. R. Linkmeyer and H. Hoyermann[42] find that the addition of about 2% of organic substances containing amide or imide groups has the effect of reducing the rate of ripening of viscose solutions so that they remain for several weeks suitable for spinning.

P. Minck[43] has patented spinning cuprammonium solutions into a caustic soda bath containing copper carbonate.

With regard to the mechanical side of the manufacturing process, C. L. Stulemeyer[44] claims the use of molybdenum for the construction of spinning nozzles, and M. Denis[45] describes an arrangement for spinning, washing, and drying viscose threads in one operation, the thread being carried forward by a travelling metallic web.

The necessity for a process of Deutsche Gasglühlicht A.-G.[46] is not obvious; they propose to load artificial silk with oxides of cerium, lanthanum, and didymium obtained from the by-products of thorium manufacture, a process which may be not unjustly regarded as painting the lily.

Glanzfäden A.-G. have made several applications relating to the manufacture of a dull artificial fibre suitable for use as a wool or cotton substitute; one of these[47] relates to a method of keeping a regenerated cellulose yarn under a very slight tension during the manufacturing process by means of sprays of the various liquids employed. The other applications describe steps in a process for manufacturing a dull yarn from a viscose which has had a minimum of alkaline treatment and ripening, a small quantity (5% on the cellulose) of glucose being added to prevent oxidation of the cellulose.

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[39] G.P. 305,577; *J.*, 1920, 13A.

[40] *Neue Faserstoffe*, 1919, **1**, 121, 266; *J.*, 1919, 895A; 1920, 329A.

[41] U.S.P. 1,316,854; *J.*, 1920, 263A.

[42] G.P. 312,392; *J.*, 1920, 227A.

[43] U.S.P. 1,317,306; *J.*, 1920, 103A.

[44] E.P. 142,038; *J.*, 1920, 444A.

[45] U.S.P. 1,317,306; *J.*, 1920, 103A.

[46] E.P. 116,103; *J.*, 1920, 595A.

[47] G.P. 312,304; *J.*, 1920, 13A.

No advance in the manufacture of staple fibre appears to have been recorded during the year, and the publications with reference to paper-yarn consist mainly of articles of a popular nature, and patents for softening, sizing, and waterproofing the finished thread.

TEXTILE FABRICS.

Most of the published work has been carried out in connexion with the use of textiles for balloon and aeroplane fabrics; some of the results, however, are of considerable interest and value, and are applicable to all cases in which these materials are exposed to light and weather. A. J. Turner[48] gives detailed results, with a large number of curves, showing the effect of weathering on the tensile strength of textile fabrics used for aeroplane and balloon purposes. The figures show that the principal cause of deterioration is light. It is most efficient in the presence of oxygen, although a measurable deterioration is produced in a vacuum; the presence of moisture does not affect the result. The active radiations lie below 3660 A.U. and visible light appears to have little, if any, destructive effect; coating with a special pigment varnish known as P.C. 10, reduced the rate of deterioration to about one-sixth. The rate of loss of strength is approximately exponential and amounted to about 72% in a sample of linen after five months, the loss being as much as 20% in one summer month.

The order of resistance to weathering under most climatic conditions is, cotton, linen, ramie, jute, silk; at Malacca, flax was found to be superior to cotton owing apparently to the humidity favouring fungal or bacterial action in the case of the latter.

An interesting observation is that coarse fabrics are much more resistant than fine ones, due to the small penetrating power of the radiations of short wave-length, which suggests that the yarn used should be as heavy as the character of the cloth will permit. Although moisture itself has no important effect in causing deterioration, the resistance to moisture undergoes a complete change when the cloth has been weathered for a considerable length of time, and instead of becoming stronger when wetted, the material shows a loss of strength ranging up to 33%.

Observations were also made as to the effect of waterproofing on weathering from which it appeared that cuprammonium treatment increased the rate, while oil, bitumen, and basic aluminium acetate had very little influence.

[48] *J. Soc. Dyers and Col.*, 1920, **36**, 165; *J.*, 1920, 512A.

A fact brought out by this work, which is of general interest to textile chemists, is the great sensitiveness of silk to ultra-violet light as compared with cellulose fibres, the former losing 47% of its strength in 15 days, and the latter only 15% in 30 days. This point was commented upon in a discussion which followed the reading of the paper, and in reply the author stated that the tests were made with pure net silk.

L. Vignon[49] has also carried out work on the same problem but with somewhat contrary results. He finds that exposure to sunlight for 270 hours causes a reduction of 20% in the strength of both linen and silk, and that exposure to ultra-violet rays 0·3 m. from a Heraeus lamp for 72 hours causes a reduction of 17% in the case of silk and 18% in the case of linen. His figures are not altogether consistent, and he appears to come to the conclusion that silk is more resistant than linen to the influence of weather and ultra-violet rays.

B. S. Levine and F. P. Veitch[50] describe a method of testing the liability of fabrics to mildew based on incubation under standard conditions, with and without inoculation.

L. Clément and C. Rivière[51] have applied Chèvefy's dynamometer to the testing of aeroplane fabrics doped with various varnishes.

The permeability of balloon fabrics has also received attention. J. D. Edwards and S. F. Pickering[52] describe a test for determining the rate at which hydrogen passes through a sample of material. The gas diffuses into a stream of carbon dioxide, which is absorbed in caustic soda, and the residual hydrogen is determined in an explosion pipette. R. T. Elworthy and V. F. Murray[53] have determined the relative permeability to helium and hydrogen of rubber-treated and skin-lined fabrics.

As artificial wool and staple fibre are now coming within the range of commercial fibres, a method proposed by P. Krais and K. Biltz[54] for the determination of vegetable fibre in the presence of wool may be of interest. They dissolve out the cellulose by a cuprammonium solution, prepared under standard conditions, which is stated to dissolve only 0·42% of the wool.

LULOSE.

The chemistry of cellulose has attracted considerable attention during the year, partly arising from Pictet's work on *l*-glucosan, and partly from the increased interest in colloid chemistry. A certain number of publications are due to the importance assumed by the various nitrates during the war. The subject generally has been dealt with by C. F. Cross in his three Cantor Lectures,[55] and F. Sproxton[56] gives a very interesting *résumé* of some recent work on cellulose plastics, from the colloidal point of view, and on the nature of cellulose itself.

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[49] *Comptes rend.*, 1920, **170**, 1322; *J.*, 1920, 481A.

[50] *J. Ind. Eng. Chem.*, 1920, **12**, 139; *J.*, 1920, 292A.

[51] *Chim. et Ind.*, 1920, **3**, 440; *J.*, 1920, 481A.

[52] *J. Ind. Eng. Chem.*, 1919, **11**, 966; *J.*, 1919, 895A.

[53] *Trans. Roy. Soc. Canada*, 1919, **13**, III., 37; *J.*, 1920, 541A.

[54] *Text. Forsch.*, 1920, **2**, 24; *J.*, 1920, 512A.

The considerable change in the chemical properties of cellulose which is caused by mechanical treatment is the subject of several papers by C. G. Schwalbe,[57] who gives further details regarding the preparation of cellulose mucilage, points out that the ease of preparation varies with the degree of chemical breakdown of the material, and discusses the relationship of the hydrated product to known forms of oxycellulose and hydrocellulose. In further papers with E. Becker,[58] he discusses methods of determining the extent to which the treatment has been carried, and the moisture content of the air-dry product. A similar change is dealt with by C. F. Cross,[59] who describes the result of trying to reproduce the conditions which gave the broken-down cellulose powder referred to in last year's Report[60]; a sample of cloth was damped and beetled until the structure was destroyed, the temperature rising to 200°. The product, however, showed α-cellulose 78·0% and β-cellulose 4·9%, and was obviously not identical with the powder in question.

The physical side of the subject is also dealt with by B. Oddo[61] who has studied the extent to which various gases are absorbed by cellulose; this is surprisingly large in some cases, and dry hydrochloric acid gas is held so strongly as to suggest the existence of a compound $(C_6H_{10}O_5)_4.HCl$. The volume of gas absorbed varies very considerably and in the following order: NH_3, HCl, SO_2, H_2S, N_2O, CO_2, C_2H_2, CO, O_2, N_2, CH_4, H_2. P. Rona and L. Michaelis[62] have determined the absorption of various liquid and solid substances. In the case of non-electrolytes they find very slight absorption even in the case of extremely surface-active substances such as *n*-octyl alcohol. They appear to ascribe most of the adsorption of electrolytes to the traces of inorganic substances, but experience in connexion with the dyeing of cellulose is hardly likely to encourage one to accept this conclusion.

A research which may lead to results of extreme importance, and which already has produced some most interesting observations, is that of W. H. Gibson,[63] who has improved on Ost's original method and has applied to various forms of cellulose a process, devised with the assistance of L. Spencer and R. McCall, for determining the viscosity of a solution prepared under standard conditions in a cuprammonium solvent. He shows that the degree of breakdown caused by the soda boiling process is reflected in the viscosity of the solutions both of the cellulose and of the nitrate prepared from it. Different viscosities are also shown by celluloses prepared from cottons of different origin but subjected to the same chemical purification. The extent to which sunlight acts in reducing the viscosity of a cuprammonium solution is worth noting. Ten minutes' exposure to bright sunlight was found to cause a fall in viscosity of a given solution from 1376 to 191 (water=1).

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[55] *J.*, 1920, 124R.

[56] *Third Report of Brit. Assoc. on Colloid Chemistry*, p. 82.

[57] *Z. angew. Chem.*, 1919, **32**, 355; *Chem.-Zeit.*, 1920, **44**, 458; *J.*, 1920, 58A.

[58] *Z. angew. Chem.*, 1920, **33**, 57, 58; *J.*, 1920, 330A.

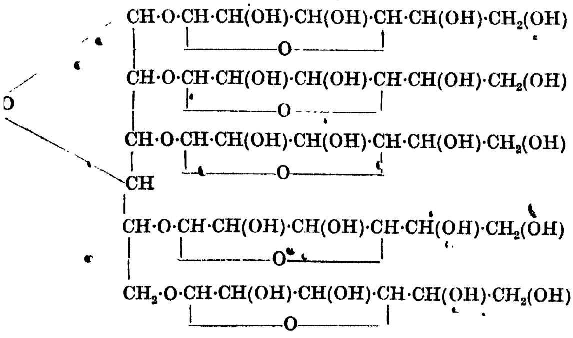
[59] *J. Soc. Dyers and Col.*, 1919, **35**, 271; *J.*, 1920, 58A.

[60] *Ann. Repts.*, 1919, **4**, 121.

[61] *Gaz. Chim. Ital.*, 1919, **49**, II., 127; *J.*, 1920, 12A.

[62] *Biochem. Zeits.*, 1920, **103**, 19; *J.*, 1920, 594A.

During the last few years, treatment of the subject of cellulose has become more and more "colloidal" and it is quite a refreshing change to find a number of papers dealing with the subject from a strictly chemical point of view, and upholding the idea that the atoms are arranged in some definite groupings which are related to the chemical properties of the compound. The idea of cellulose being a condensed glucose anhydride has found favour with many workers; Tollens for example proposed a formula in which the units are connected together in a chain by a double oxygen linking at the aldehyde groups. K. Hess and W. Wittelsbach,[64] however, put forward another view, which they base on Fischer's formula for the tannins, and which involves the idea of a glucose-glucoside. A number of alternatives of this class are considered and the one they prefer is a pentaglucosidyl-glucoside as follows:



The ground on which this is selected is that

give four molecules of monose to one of biose, which agrees fairly well with the proportion of glucose to cellobiose obtained on acetolysis. They find further support in the proportion of ethoxyl observed in the products of acetolysis of a sample of ethyl-cellulose, which gives a series of dextrins with ethoxyl content gradually decreasing as the reaction proceeds, under conditions chosen so as to avoid hydrolysis of ethoxyl groups themselves. With regard to the way in which these units are linked together the authors' views appear somewhat indefinite, since while stating clearly that they are of the opinion that the combination is by means of residual affinity, in another part of the paper they admit the possibility of several units being connected together by a cellobiose group. The principle involved in this work, which is of considerable interest, may lead to results of some value, and it is to be hoped that the authors will be able to carry out their intention of further investigating these series of substituted acetolysis products. The work, however, is hardly advanced sufficiently to justify the confidence with which their formula is put forward, and the development of their theory appears to have obscured certain observations which point to the necessity for some modification of their views. A unit group such as their "celluxose" which has the formula $(C_6H_{10}O_5)_6.H_2O$ without further condensation could not possibly give anything approaching cellulose in composition by a combination of residual affinities; Boeseken, v. den Berg, and Kerstjens,[65] for instance, who also considered the question of cellulose being a hexose anhydride $(C_6H_{12}O_6)n-(n-1)H_2O$, from a study of the degree of acetylation of the original material and of its hydrolysis products, found values for *n* as high as 47·5. The Hess and Wittelsbach formula offers no explanation of several difficulties that present themselves in the case of any glucose-anhydride scheme; it has been stated that glucose does not give any appreciable yield of either bromomethylfurfural or *l*-glucosan, and although it is quite likely that some form of anhydride condensation would turn the decomposition in this direction there is no evidence to this effect. Two recent papers throw some light on this point; A. Pictet and H. Goudet[66] have examined several common glucosides and have isolated *l*-glucosan in each case; while P. Karrer,[67] taking these results into consideration with the fact that *α*-glucose has only yielded traces fo *l*-glucosan, suggests that cellulose contains *β*-glucosidic groups and supports his contention by the observation that *β*-glucose yields a considerable amount of *l*-glucosan. Pictet now proposes a scheme (hardly a formula) for cellulose which takes most of these observations into account, and in a lecture before the French

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[63] *Chem. Soc. Trans.*, 1920, **117**, 479; *J.*, 1920, 541A.

[64] *Z. Elektrochem.*, 1920, **26**, 232; *J.*, 1920, 512A.

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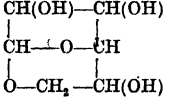
[65] *Rec. Trav. Chim.*, 1916, **35**, 320.

[66] *Helv. Chim. Acta*, 1919, **2**, 698; *J.*, 1920, 40A.

[67] *Helv. Chim. Acta*, 1920, **3**, 258; *J.*, 1920, 348A.

Chemical Society on May 21st,[68] put forward the view that cellulose contains two β-glucose groups, one α-glucose group, and one hydrofuran nucleus containing two side chains which he terms the "chitose" grouping. He appears to differ from Sarasin regarding the constitution of *l*-glucosan, to which he now ascribes the formula



The ultimate hydrolysis products of cellulose have received an addition through the work of H. Ost and R. Prosiegel,[69] who have identified a new biose "cello-isobiose" among the products of acetolysis in presence of considerable quantities of sulphuric acid. It forms fine needles, m.p.165°–190° with decomposition, $[\alpha]_D = 23°$, reduces Fehling's solution, and is not affected by yeast, but is hydrolysed to dextrose by hydrochloric acid.

E. Knecht and L. Thompson[70] have investigated the properties of a highly oxidised cellulose obtained by treatment with an acid solution of potassium permanganate. The product had a copper number of 14·2, which is about twice as high as that of the oxycellulose obtained by Nastjukov with bleaching powder.

The Power Gas Corporation, Ltd. and H. Langwell[71] have worked out a process for the direct conversion of cellulose into acetic acid, at temperatures between 25° and 60° C., using a symbiotic mixture of bacteria obtained from fermenting vegetable matter. A similar decomposition is described by G. J. Fowler and G. V. Joshi,[72] who inoculated cellulose with mud from a septic tank and identified acetic acid and methane among the products. What is probably the first stage in these changes has been investigated by Hutchinson and Clayton,[73] who have isolated an aërobic bacterium *Spirochaeta cytophaga* which attacks cellulose forming a mucilage. Its growth is inhibited by soluble carbohydrates.

Cellulose Esters.

Several patents have appeared dealing with the manufacture of cellulose acetate. E. Wagner[74] proposes to conduct the acetylation in two stages, by doing which a saving in acetic anhydride and catalyst is effected; W. G. Lindsay[75] impregnates cellulose with benzene and alcohol and then acetylates with a mixture of acetic anhydride and benzene; and J. O. Zdanowich[76] proposes to form chloro-acetic acid catalysts *in situ* by passing chlorine into the acetylating mixture. The patent refers to the nascent state of the chloro-acetic acids formed, but it is probable that any increased activity observed is due to the formation of hydrochloric acid during the substitution of chlorine for the hydrogen of the acetic acid.

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[68] *Bull. Soc. Chim.*, 1920 **27**, 641 *seq.*

[69] *Z. angew. Chem.*, 1920, **33**, 100; *J.*, 1920, 421A.

[70] *J. Soc. Dyers and Col.*, 1920, **36**, 251; *J.*, 1920, 718A.

[71] E.P. 134,265; *J.*, 1920, 38A.

[72] *J.*, 1920, 93B.

[73] *La Papeterie*, 1920, **42**, 409.

[74] G.P. 299,181; *J.*, 1920, 400A.

[75] U.S.P. 1,338,661; *J.*, 1920, 445A.

C. F. Cross has contributed a note to the Society of Dyers and Colourists,[77] in which he points out that the primary cellulose acetates prepared by the Dreyfus processes do not support the generalisations of Ost,[78] in that they are not soluble in chloroform and can be redissolved an indefinite number of times in acetone. He also states that the properties of the Mork products, which are soluble both in acetone and in chloroform, do not agree with Ost's suggestions. The subject of acetate solutions generally is dealt with by H. J. H. Fenton and A. J. Berry[79] who, in discussing the suitability of various solvents for doping purposes, arrive at the conclusion that the chemical constitution of a liquid does not give any indication of its solvent properties for cellulose acetate, and that its behaviour in this respect is more closely related to the dielectric constant. G. Barr and L. Bircumshaw in a discussion before the Faraday and Physical Societies on October 25th, 1920,[80] described the results of viscosity tests with solutions of acetates in mixtures of acetone with water, benzene, or alcohol.

The solubility of the cellulose nitrates, which was the subject of a large amount of research during the war, is dealt with in several papers mostly from the point of view of the viscosity of the solutions. For such purposes E. F. Higgins and E. C. Pitman[81] prefer Stormer's viscosimeter, which depends on measurement of the frictional resistance to rotation, to either the efflux or steel ball viscosimeter. J. Duclaux and E. Wollman[82] find that, by fractional precipitation with water from acetone solution, they are able to separate a sample into fractions of the same nitrogen content but differing in viscosity as much as 46 : 1.

I. Masson and R. McCall[83] have determined the proportions of acetone and water which give the maximum solvent effect as indicated by a minimum viscosity of the resulting solution. These mixtures contained from 6 to 10% of water, and varied with the

[76] E.P. 139,232; *J.*, 1920, 483A.

[77] *J. Soc. Dyers and Col.*, 1920, **36**, 19.

[78] *Ann. Repts.*, 1919, **4**, 122.

[79] *Proc. Camb. Phil. Soc*, 1920, **20**, 16; *J.*, 1920, 624A.

[80] *Cf. J.*, 1920, 376R.

[81] *J. Ind. Eng. Chem.*, 1920, **12**, 587; *J.*, 1920, 541A.

[82] *Bull. Soc. Chim.*, 1920, **27**, 414; *J.*, 1920, 528A.

[83] *Chem. Soc. Trans.*, 1920, **117**, 819; *J.*, 1920, 641A.

degree of nitration. A similar method has been applied to solutions of cellulose nitrate in ether-alcohol mixtures by W. H. Gibson and R. McCall[84] who find in this case also that the optimum ratio is not affected by the concentration of the solution but varies with the nitrogen content of the material.

F. Sproxton, in a paper read before the Faraday and Physical Societies, on the occasion previously referred to,[80] discussed these results, and expressed the opinion that a nitrocellulose-water complex is formed which dissolves in a molecular complex of the solvent liquids. These papers were also discussed by Sir Robert Robertson at the same meeting from the point of view of the manufacture of explosives.

As usual, patent literature during the year has contained a large number of additions to the list of organic substances proposed as plasticising or softening agents. These include toluene and xylene monoalkyl-sulphonamides, phenyl salicylate, *o*- and *p*-hydroxybenzyl alcohols, diethyl tartrate, β-naphthol amyl ether, resorcinol monoacetate, chloronaphthalene, naphthalene, and anthracene oil. The following substances, which may be more strictly described as solvents, have also been suggested: Furfural, ethyl propionate, and a mixture of acetaldehyde, isobutyl acetate, and acetic acid.

WOOD.

A publication of the U.S. Forest Products Laboratory[85] describes the results of the measurement of many thousand wood fibres It is shown that the fibre length cannot be used to identify the material, since in one tree the fibres vary more than do the averages of different species. For example, one disc of Douglas fir showed a range of from 0·8 to 7·65 mm., while the averages for Douglas fir and longleaf pine were 4·41 and 3·67 mm. respectively. In the first case 67% of the fibres lay between 4·5 and 6·5 mm., which represents what is usually described as the "average fibre length." During the first 20 to 50 years of growth the increase in fibre length towards the outside of the tree is very striking, but after this there is not much change even up to 400 years. The spring fibres are longer than those formed later in the year and there is also a perceptible increase in length for about two-thirds of the height o the tree.

Considerable progress has been made in our knowledge of th composition of wood and methods for its determination; processe are now available which give a total of approximately 100%, bu there is still a slight amount of overlapping, and the difficult question of the lower hemicellulosic constituents requires further work.

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[84] *J.*, 1920, 172T.

[85] *Technical Notes*, March 1, 1920.

W. H. Dore[86] has modified his scheme for the analysis of coniferous woods by omitting the alkaline hydrolysis and by determining the mannan and galactan, which he finds amount together to about 5%. Where the deciduous woods are concerned he finds it necessary[87] to use König and Becker's hydrochloric acid method for determining the lignin, and further extends his scheme by employing extractions with cold water and cold 5% caustic soda solution subsequent to the determination of resin. The use of caustic soda at this stage is open to question as there is reason to suppose that it may hydrolyse acetyl groups and also extract the lower cellulose hydrates, besides which it is not yet proved that an extraction with boiling water leaves any non-cellulosic substances other than lignin.

With reference to the determination of cellulose, S. A. Mahood[88] discusses the influence of the state of division of the wood on the percentage of cellulose found, and also the effect of the modifications proposed by Johnsen and Hovey and by Sieber and Walter, both of which give lower results than the original method of Cross and Bevan. He finds for example :—

	Johnsen and Hovey.	Sieber and Walter.	Cross and Bevan (Schorger apparatus).
	%	%	%
I.	46·21	50·90	52·49
II.	50·46	53·37	56·78

and considers that the two former methods give an excessive attack on the cellulose. W. H. Dore,[89] dealing with the same subject, is also of the opinion that preliminary hydrolytic treatments are undesirable and suggests that, instead of attempting to remove the lower celluloses before the lignin, the best method of determining them is by applying Cross and Bevan's separation with 17·5% caustic soda to the total residual cellulose. He gives figures showing that the α-cellulose obtained in this way is practically free from furfural residues, and prefers the Renker-Sieber–Walter modification of Cross and Bevan's original method for cellulose determination. It should be noted, however, that in a paper previously referred to,[86] which is of later date, he adopts an extraction with cold 5% caustic soda solution previous to the determination of the lignin.

The literature dealing with the subject of lignin increases in bulk and complexity. E. Hägglund[90] discusses the isolation of lignin by various methods, and gives results of an investigation of the product obtained from pine wood by separation with 43%

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[86] *J. Ind. Eng. Chem.*, 1920, **12**, 476 ; *J.*, 1920, 513A.
[87] *J. Ind. Eng. Chem.*, 1920, **12**, 984 ; *J.*, 1920, 778A.
[88] *J. Ind. Eng. Chem.*, 1920, **12**, 873 ; *J.*, 1920, 718A.
[89] *J. Ind. Eng. Chem.*, 1920, **12**, 264 ; *J.*, 1920, 400A.
[90] *Ark. Kemi, Min., o. Geol.*, 1918, **7**, 1 ; *J.*, 1919, 895A.

hydrochloric acid. It yields 14·39% of methoxyl and 3·69% of furfural but appears to have lost acetyl groups in the separation as it gives lignic, formic, and protocatechuic acids on potash fusion. It is stated to be only slightly soluble in calcium bisulphite solution, which suggests that it has undergone considerable alteration during the process of isolation.

M. Hönig and W. Fuchs[91] find that on fusion of barium ligninsulphonates with caustic potash at 250°–300° C. a yield of 13–19% of protocatechuic acid is obtained. In a later paper[92] they state that on boiling with barium hydroxide solution these salts give unidentified insoluble substances and a soluble salt $C_{18}H_{30}O_{10}SBa$, which appears to be derived from a tannic acid of the catechu group and gives a good yield of protocatechuic acid on fusion with caustic potash.

P. Klason[93] gives the results of further investigation of naphthylamine ligninsulphonate and is of the opinion that its formation is due to the presence of the grouping R. CH : CH. CHO, which may be to some extent formed by atmospheric oxidation of R. CH : CH. CH_2·OH present in fresh sulphite liquor. He concludes that lignin is largely composed of coniferyl aldehyde and alcohol.

C. G. Schwalbe and E. Becker[94] have investigated the differences observed in the composition of alder wood of various ages. As the age increases the proportions of pentosan and acetic acid decrease while the lignin and cellulose both give higher figures. The proportion of lignin is greater in the heart wood than in the sap wood. The authors criticise the results of H. Pringsheim and H. Magnus,[95] who reply[96] by casting doubts on the sufficiency of Schwalbe and Becker's process for determining acetic acid, but the method, that they prefer, of heating the wood for six hours with eight times its weight of 3·5% sodium hydroxide solution under 6 atm. pressure appears to be too drastic to afford evidence of the presence of acetyl groups as such. Schwalbe and Becker reply[97] that not more than one third of the total acetic acid is derived from the lignin, a figure which is in agreement with that of W. H. Dore,[98] who has studied the distribution of acetic acid and furfural between the cellulose and the lignin in redwood, and finds that the greater part of the acetic acid is associated with the cellulose. He boils the material for three hours with 2·5%

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[91] *Monatsh.*, 1919, **40**, 341; *J.*, 1920, 330A.

[92] *Monatsh.*, 1920, **41**, 215; *J.*, 1920, 719A.

[93] *Ber.*, 1920, **53**, 706; *J.*, 1920, 482A.

[94] *Z. angew. Chem.*, 1920, **33**, 14; *J.*, 1920, 185A.

[95] *Ann. Repts.*, 1919, **4**, 126.

[96] *Z. angew. Chem.*, 1920, **33**, 56; *J.*, 1920, 263A.

[97] *Z. angew. Chem.*, 1920, **33**, 225; *J.*, 1920, 718A.

[98] *J. Ind. Eng. Chem.*, 1920, **12**, 472; *J.*, 1920, 513A.

sulphuric acid, a process which is practically identical with that of Schwalbe and Becker.

H. Wichelhaus[99] has obtained substances from the distillation of wood with steam at about 205° C., to which he assigns the formulæ $C_{10}H_{22}O_9$ and $C_{16}H_{22}O_{11}$, and suggests that they are related to brasilein and hæmatoxylin.

Several patents have appeared for the production of sugars etc. from wood by chemical processes. C. G. Schwalbe[100] claims that it is possible by first treating damp wood with gaseous hydrochloric acid and then by hydrolysing with dilute acid in the ordinary manner, to obtain 70% of soluble matter, mainly dextrose and pentose, calculated on the weight of wood taken. Zellstoff-Fabrik Waldhof and V. Hottenroth[101] effect a preliminary hydrolysis with sulphuric acid of about 80% strength, under conditions which do not result in solution of the cellulose, and then dilute and boil. The excess of sulphuric acid may be removed by dialysis through a copper ferrocyanide membrane. Zellstoff-Fabrik Waldhof and H. Clemm[102] have an alternative method in which the sulphuric acid is neutralised by ammonia, the bulk of which may be recovered by evaporation and crystallisation.

WOOD PULP.

The prospect of a shortage of raw material, which has been referred to in previous reports, grows more imminent, but the number of new vegetable materials proposed is falling off. The publications in this connexion have been mainly concerned with the conservation of present resources and the better treatment of materials already suggested.

The enormous amount of wood annually destroyed by forest fires is receiving serious attention, and the use of aeroplane patrols for detecting and giving notice of these in their early stages is developing with considerable success. It is reported that in the United States a distance of over 200,000 miles was covered between June and October, 1919, and that 442 fires were observed.

The action of the Canadian Government in prohibiting the export of un-pulped wood from Crown lands has resulted in a certain amount of disappointment in interested circles in the United States, and a proposition for the utilisation of Alaskan timber has been discussed, but opinion is divided as to the commercial value of this material.

The principal new raw materials suggested are in Mexico the tree "cuahalose,"[103] in Morocco the "doum," *Chamœrops*

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[99] *Ber.*, 1919, **52**, 2054; *J.*, 1920, 59A.

[100] G.P. 305,690; *J.*, 1920, 346A.

[101] G.P. 309,150, 310,149, 310,150; *J.*, 1920, 204A.

[102] G.P. 305,180; *J.*, 1920, 203A.

[103] *Le Papier*, 1919, **22**, 175.

humilis,[104] and in Brazil "anhinga."[105] C. J. West[106] gives a condensed account of articles by C. F. Juritz on the suitability of a large number of African grasses for paper manufacture.

In France the amount of work being done on this subject is considerable. The French school of paper-making at Grenoble has published[107] a bibliography which is well worth consultation by those interested in the manufacture of cellulose from vegetable material. L. Vidal[108] gives a description of pulp obtained on a small scale by the soda process from sycamore, *Platanus orientalis*, which he considers a very promising material; the microscopic appearance of the fibres is described and illustrated. In another publication[109] he reviews the problem of the supply of raw materials for paper-making, and J. M. de Portement[110] discusses the same subject and the question of re-afforestation. M. Barbillion contributes an article[111] on the raw material available in the French colonies, and is of the opinion that bamboo is the most promising in view of Raitt's process for crushing the knots before boiling, although even then the consumption of soda is rather high. This principle is employed by E. Arnould,[112] who applies a similar process to the production of pulp from esparto. A bacterial process for the treatment of esparto has been devised by Dubrot.[113]

The importance of the question of decay both in wood and in pulp continues to be recognised, and F. J. Hoxie[114] gives a list of the principal fungi that attack pulpwood, illustrated with photographs showing their appearance and manner of growth. *Lenzites sepiaria* and *Fomes roseus* occur in spruce hemlock and pine, *Fomes hirsutus* in poplar, *Polyperous pargamenus* in birch and *Caratostamella pilifera* in the sapwood of most pulpwoods. This latter is the cause of the common blue stain in sapwood but does not rot the fibre to a serious extent. He finds that fungoid growth is most active between moisture limits of 20 and 50%, and suggests keeping the proportion of water either above or below this range. R. J. Blair[115] deals with the same subject and also its extension to finished pulp. F. Barnes[116] reprints an earlier article with illustrations of fungi observed in various pulps.

[104] *Le Papier*, 1919, **22**, 193.
[105] *Paper*, 1919, **25**, 707.
[106] *Paper*, 1920, **26**, [16,] 10.
[107] *La Papeterie*, May 25, 1919; *Paper*, 1919, **25**, 1104.
[108] *La Papeterie*, 1920, **42**, 434.
[109] *Chim. et Ind.*, 1919, **2**, 730.
[110] *Le Papier*, 1919, **22**, 321.
[111] *Paper*, 1920, **26**, [21,] 11.
[112] *Le Papier*, 1919, **22**, 344.
[113] *La Papeterie*, 1920, **42**, 203.
[114] *Pulp and Paper Mag.*, 1920, **18**, 105, 267.
[115] *Pulp and Paper Mag.*, 1920, **18**, 451.
[116] *Pulp and Paper Mag.*, 1920, **18**, 995.

S. A. Mahood and D. E. Cable[117] have analysed a sample of infected mechanical pulp in which the fungus *Paxillus panuoides* was identified; the decomposition had not proceeded very far, but the alteration in composition clearly pointed to selective attack on the cellulose. The effect of these changes on the quality and working properties of the same sample has been studied by O. Kress, C. J. Humphrey, and C. A. Richards.[118] The infected pulp was found to be inferior in every respect, it was short-fibred, too free, gave a dark-coloured product of poor strength and low yield, and gave trouble by sticking to the rolls and by foaming.

No development of outstanding novelty and importance has been recorded in the boiling process; a number of devices for ensuring more regular working, and discussions of present practice have been published in technical journals. The advantages of using liquid sulphur dioxide are described by V. P. Edwardes,[119] and G. K. Spence[120] gives the results of adding sulphur to a soda boiling liquor. The quantity employed was 1·1 lb. per 100 lb. of stock, and as the quantity of bleach saved was only 0·92 lb. of 35% bleaching powder there appears to be very little advantage in the process pending the results of further experiments to determine whether there is any improvement in yield and strength.

Zellstoff-Fabrik Waldhof, H. Clemm, and R. Wilstätter[121] propose to obtain the advantages of a high pressure during digestion, without the disadvantages of a corresponding temperature, by forcing a liquid or gas into the digester. An arrangement of coils for indirect heating is described by R. H. Hult[122] and direct heating is dealt with by J. K. Ruths and Akt. Vapor-ackumulator.[123] M. Müller[124] claims that the addition of organic salts such as calcium acetate, especially in the presence of calcium phenolate, has a favourable effect on alkaline digestion. A. Franz[125] describes a technical process somewhat similar to Cross and Bevan's cellulose separation, in which he digests with chlorine in an inert solvent such as carbon tetrachloride and then with 2% caustic soda solution.

Waste Liquor.

A. Klein[126] has compiled an abstract of recent work which forms a useful supplement to the book of Johnsen and Hovey referred to in last year's Annual Report.

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[117] *Paper*, 1920, **25**, 1149.

[118] *Paper Maker's Monthly J.*, 1920, **58**, 8.

[119] *Pulp and Paper Mag.*, 1920, **18**, 825.

[120] *Paper*, 1920, **26**, 19; *J.*, 1920, 686A.

[121] G.P. 304,214; *J.*, 1920, 60A.

[122] U.S.P. 1,337,704; *J.*, 1920, 445A.

[123] E.P. 144,084; *J.*, 1920, 541A.

[124] G.P. 323,743; *J.*, 1920, 745A.

[125] G.P. 323,936; *J.*, 1920, 745A.

[126] *Pulp and Paper Mag.*, 1920, **18**, 1067.

The problem of dealing with waste liquor is evidently attracting a number of ingenious enthusiasts but some of the suggestions are so incompatible that their utility must be looked on with suspicion. During the year various publications have asserted its suitability for the manufacture of adhesives, lubricants, insecticides, binding material for road-making, size for paper, and as a catalyst for rubber manufacture.

J. S. Robeson[127] proposes to employ it in the manufacture of a sulphide dyestuff by removing the calcium and heating with sulphur and an alkali sulphide.

Among the methods of treatment that are gradually establishing their practical value, employment as fuel is dealt with by H. K. Moore[128] from the point of view of the explosion process. He gives an extensive series of thermochemical data referring to this process, which consists in neutralising with salt-cake, heating to a high temperature, and then allowing the superheated liquor to expand into a boiler flue, thus evaporating the water and burning the finely pulverised residue.

With regard to the production of alcohol, two proposals for effecting the removal of sulphur dioxide before fermentation are those of O. Schaeffer[129] who claims passing the liquor directly from the digester in a thin film over steam-heated coils in a vacuum, and of R. H. McKee[130] who passes it down a tower against a current of steam, evaporates the liquor to half its bulk, cools, ferments while bubbling air through the liquid, and removes the last traces of sulphur dioxide by distilling in the presence of a dilute solution of soda ash. A detailed cost sheet shows a total cost of 28·4 c. per U.S. gallon, which may be reduced by about one half if account is taken of the heat values obtained by evaporating and burning the residue in the boilers.

L. Akerblom[131] describes a method of separating cymene from the distillation products of a sulphite digestion. It appears that there is a demand for this substance for the manufacture of thymol which at present commands a high price.

A process of H. F. Weiss[132] may lead to the recovery of valuable products in the operation of grinding mechanical pulp. He separates the water from the freshly ground pulp and returns it to the grinding operation until the concentration of soluble substances is high enough to render their separation profitable.

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[127] U.S.P. 1,316,742; *J.*, 1919, 894A.

[128] *Paper*, 1920, **25**, 1157, 1197, 1241; *J.*, 1920, 444A.

[129] U.S.P. 1,342,721.

[130] *Pulp and Paper Mag.*, 1920, **18**, 715; *J.*, 1920, 594A.

[131] U.S.P. 1,333,694; *J.*, 1920, 361A.

[132] U.S.P. 1,339,489; *J.*, 1920, 482A.

PAPER.

The use of cotton hull fibre has been further investigated by O. Kress,[133] who describes in detail experimental cooking of the fibre, its manufacture into paper, and the properties of the products. It is obvious that the last word has not been said on this subject but the results are very encouraging. In most cases the fibre papers were inferior in strength to those containing a corresponding proportion of rag, but the author is strongly of the opinion that the beating conditions are capable of considerable improvement. The results lend further support to the suggestion made in his previous paper with S. D. Wells[134] that as large a proportion as possible of the hull particles should be mechanically removed before boiling; failing this a hard brush during washing in a beater appears necessary. This last treatment is also desirable in order to get sufficient hydration. As far as the actual manufacture into paper is concerned, beating, screening, sizing, and drying proceeded normally and offered no difficulty. The product showed itself particularly suitable for the manufacture of blotting paper and forms a good substitute for soft rag stock for most purposes.

Visual estimation of the percentage of the different fibres present in a sample of paper is growing in favour. This method is recommended by R. C. Griffin[135] who recommends comparison with slides of known composition, and another writer points out[136] that, owing to the loss of lignin without alteration of volume in the digestion process, there is a tendency to over-estimate the weight of sulphite in admixture with mechanical pulp, so that an empirical correction varying from 10 to 30% of the sulphite pulp observed should be deducted from the estimated proportion of sulphite and added to that of the mechanical pulp. F. B. Seibert and J. E. Minor[137] describe a refinement of the method which consists in rendering the degree of lignification more easily recognisable by counter-staining with malachite green and Congo red. No difference can be detected by this modification between soda and bleached sulphite pulps. A somewhat similar method, which might be useful for this purpose, has been proposed for the identification of lignocellulose in cotton by F. L. Barrett[138] who recommends discharging the colour of the non-lignified cellulose with a weak bleach instead of counter-staining with a direct dye.

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[133] *Paper*, 1920, **25**, 964, 1009; *J.*, 1920, 263A.
[134] *J.*, 1919, 858A.
[135] *J. Ind. Eng. Chem.*, 1919, **11**, 968; *J.*, 1919, 895A.
[136] *Pulp and Paper Mag.*, 1919, **17**, 948; *J.*, 1920, 12A.
[137] *Paper*, 1920, **25**, 1005.
[138] *J.*, 1920, 81T.

S. Smith[139] has investigated the bearing of the ratio of viscosity to specific gravity of water at different temperatures on the rate of draining of paper pulp. He finds that as the temperature rises the rate of draining increases faster than the theory indicates. It is suggested that this effect is due to dehydration of the fibres causing an increase in the size of the capillaries.

The method of growth of dendritic markings in paper is the subject of a careful micro-chemical study by J. Strachan[140] who arrives at the conclusion that they are caused by particles of alloys containing copper which are first attacked by sulphuric acid from aluminium sulphate, and that the copper sulphate so formed then creeps along the fibres and is subjected to alternate reduction and oxidation.

Beating.

With regard to the beating operation, the influence of the consistency of the stock and the design of the apparatus on the efficiency and power consumption is dealt with by W. B. Campbell.[141] He refers to the hydrating effect produced by the friction of the fibres on each other; a patent of interest in this connexion is that of A. Courrier[142] who has designed a machine to make special use of this action. A recent publication[143] discusses the effect of the inertia of the stock on the ratio of width to length in beater construction, and the advantages to be gained by employing several compartments with propellers to assist circulation. T. H. Nash[144] proposes to mount a series of rolls in a common trough with arrangements for regulating the number of times the pulp passes under the rolls. J. G. Varlot[145] also deals with the theory of beater design, in this case from the point of view of the working area of the bedplate.

The effect of mechanical treatment on the production of cellulose mucilage has been described by Schwalbe and Becker in several papers (p. 133) and the special application of their work to the beating process is discussed by F. B. Seibert and J. E. Minor.[146] This aspect of the matter is also dealt with in a patent by Schwalbe.[147]

A. B. Green[148] has patented an instrument for measuring the viscosity of stock in the beater, which depends on the power required to rotate, at a uniform speed, a small body fitted with blades or wings and immersed in the stock.

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[139] *Papierfabr.*, 1919, **17**, 1121; *J.*, 1920, 12A.
[140] *Paper*, 1920, **26**, 890.
[141] *Pulp and Paper Mag.*, 1920, **18**, 1087.
[142] *La Papeterie*, 1920, **42**, 20.
[143] *La Papeterie*, 1920, **42**, 500.
[144] E.P. 135,733; *J.*, 1920, 60A.
[145] *Bull. Synd. Fab. Papier et Carton*, 1920, **3**, 40.
[146] *Pulp and Paper Mag.*, 1920, **18**, 939; *J.*, 1920, 686A.
[147] G.P. 319,826; *J.*, 1920, 514A.
[148] U.S.P. 1,321,736.

Bleaching.

The use of liquid chlorine is attracting some attention, and a recent article by J. Simonneau[149] advocates the use of ozone for bleaching paper pulp. He claims that the cost of this method is less than that of bleaching either by chloride of lime or by chlorine; the figures available are not very complete and it is difficult to arrive at an estimate of the exact cost.

The importance of adjusting the degree of bleaching to meet the variations that occur in boiling practice is indicated by the number of attempts to find a test for the bleaching quality of a pulp. Most of these are based on the amount of lignin present, as in the case of A. Chambovet[150] who suggests the use of the methoxyl determination, F. B. Seibert and J. E. Minor[137] who stain with malachite green and Congo red, and E. Hägglund[151] who finds that Klason's method for lignin determination gives the best indications. He also states that the copper reduction figure is no measure of the bleaching value, and that none of the usual chemical tests shows any relationship to the strength of the pulp.

P. Klemm[152] is of the opinion that for paper-making purposes it is necessary to make a series of tests with four concentrations of calcium hypochlorite solution, comparing the quantity of chlorine used up and the colour of the products.

Sizing.

The question of sizing in general is dealt with by E. Arnould.[153] A number of interesting points in connexion with the use of starch and its derivatives are brought forward by J. Traquair[154]; he discusses the influence of colloids on the condition of the rosin-alumina precipitate and states that acetylated starches such as "feculose" or "feculoid" have a colloidal value equal to glue and about four times as great as starch itself. He considers that this is due to the portions of the starch grain of high molecular weight, which are normally insoluble in water, being rendered soluble by the process of acetylation and consequently increasing the effective value of the material.

[149] *La Papeterie*, 1920, **42**, 23.

[150] *La Papeterie*, 1920, **42**, 440.

[151] *Papierfabr.*, 1919, **17**, 301 ; *J.*, 1919, 894A.

[152] *Chem.-Zeit.*, 1920, **44**, 458.

[153] *Rev. Univ. Papeterie*, 1919, ii., 7.

[154] *Paper*, 1920, **26**, 93, 185 ; *J.*, 1920, 414A.

As usual a large number of substances have been proposed as new sizing materials. These include montan wax emulsified with resin, naphthenic acid soap, or liquid resin; waste sulphite liquor; tar-aldehyde condensation products; wood-pulp resin naturally present; aluminium acetate or formate; tannery glue and sodium silicate; colloidal solutions of metallic hydroxides obtained by dialysis; glue and china clay; and sulphite-cellulose waste liquor.

O. Kamm, with F. H. Tendick,[155] has continued his work on the determination of starch in paper, and has shown that it is possible to extract tub-size, which usually consists of hydrolysed starches, by means of a 45-minute extraction with water at 60° C., and then to determine beater-starch by extraction with dilute acetic acid.

F. Stöckigt[156] has devised a test for size-fastness which appears to be more sensitive than the ink-stroke test of Herzberg. He observes the number of seconds required for the development of a pink colour when a small folded boat of the paper is floated on a 2% solution of ammonium thiocyanate and wetted with a 1% solution of ferric chloride. The relative size-fastness is obtained by dividing this figure by the gram weight per square metre and is of a similar order to the critical stroke width of Herzberg.

Testing.

Those interested in this subject should consult the Report on Paper Testing of the Technical Association of the Pulp and Paper Industry[157] which contains very full information as to the latest approved methods.

The influence of hygroscopic moisture on tensile strength has been referred to in a previous Report[158]; a more recent paper[159] deals with the same subject. J. Strachan[160] in some notes on paper testing refers to the influence that water also has on the thickness of paper and states that an error of 5% in measurement may be introduced by variations in moisture. The same author points out that the various types of bursting strength testers in use differ to a considerable extent when a number of sheets are tested together, the bursting loads found by some giving a greater ratio and by others a smaller ratio than the number of sheets tested would lead one to expect. In testing aeroplane fabrics it has been found by G. S. Heaven[161] that the ratio of bursting load to number of sheets tested depends almost entirely on the way the sheets are held in the machine.

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[155] *Paper*, 1919, **25**, 460; *J.*, 1920, 102A.

[156] *Woch. Papierfabr.*, 1920, **1**, 39.

[157] *Paper*, 1919, **25**, 693; *J.*, 1920, 225A.

[158] *Ann. Repts.*, 1917, **2**, 157.

[159] *La Papeterie*, 1919, **41**, 455.

[160] *Paper*, 1920, **27**, [9], 18.

C. F. Sammet[162] describes the construction of a modified Schopper machine for the determination of tearing strength and gives figures obtained with different types of paper. He substitutes a wooden lever arm, starts with this raised to a fixed position and allows it to fall while tearing the paper until the weight of the arm is balanced by the resistance of the paper.

P. Houslan[163] describes a Schopper machine fitted with a recording cylinder which registers the load and stretch. This was constructed for testing paper for heavy bags, and by repeatedly subjecting the paper to a load of 10% less than the breaking strain a looped curve was obtained which gave a measure of its resiliency and endurance. The results were checked by finding the number of times loaded bags could be dropped before breaking, and were found to agree very well with this practical test.

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[161] Private communication.

[162] *Paper*, 1920, **25**, 1053 ; *J.*, 1920, 330A.

[163] *Paper*, 1920, **27**, [3], 15.

BLEACHING, DYEING, PRINTING, AND FINISHING.

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PROGRESS during the year 1920 in the bleaching, dyeing, and printing industries has been rather in the direction of a better understanding of the nature of processes already existing than in the invention of processes of striking originality. The work of the Research Committees in the various branches of these industries has not yet produced any results which may be acclaimed as of outstanding merit or utility. It is no doubt too early to expect such results, and it is possible that much that has been done has been communicated privately to the subscribing firms. Still, we are tempted to question whether the association between the research laboratories and the works is sufficiently intimate. No doubt this intimacy is one which can only be of gradual growth, but there is at present a lack of obvious co-ordination which might be established to foster that growth. For example, the investigator engaged in any piece of research should be given an opportunity of observing, on the spot, existing works' practice in connexion with the subject of research, before the scope and nature of that research is defined. The form of statement of the technical problem requiring solution is frequently such as to mislead the investigator at the outset, and there is a wealth of accumulated experience and observation behind works practice of which he may remain ignorant, because it is rarely realised vividly in the minds of works' managers, much less put into the form of accurate and comprehensive statement. The task of reviewing the patent literature of the year suggests that the Research Associations might very well undertake trials of the processes described in new patents and issue reports on these, on the lines of the reports issued by the Société Industrielle de Mulhouse. Such impartial reports would be valuable both to the patentees and to those engaged in the industry. The results which the Research Associations have published during the year are not assembled together in the present review, but are quoted incidentally with other published matter on the same subjects.

The elaborate pattern cards and directions for carrying out special processes which were issued by the German dye-makers in such profusion in pre-war days, are conspicuously absent in 1920. The corresponding literature at present issued by English firms is notably meagre. The activities in the colour industry have not yet born fruit of this description. On the other hand, there are many indications that the chemical privations of the war have had a stimulating effect on dyers, and long-established processes have undergone a critical examination which has been highly beneficial

Information which was of necessity withheld during the war is being gradually disclosed, but the bulk of it is rather of historical interest than of outstanding technical utility.

GENERAL.

A paper by W. H. Nuttall[1] on "Wetting power and its relation to industry" is of special interest to dyers. The author deals very fully with the physical laws which govern the phenomenon of wetting, and although he draws his industrial examples from other industries, the application of his paper to the practice of scouring, the de-gumming of silk by the froth process, froth-dyeing, and numerous other processes will be apparent to every dyer. The paper does not lend itself to such short abstraction as could be given here, but it is full of suggestive material.

The question of regulation of imports of dyestuffs is a very burning one at the present time. The whole question has been ventilated in the Press very freely, and it is impossible to make references to all that has been published on the subject; attention may, however, be drawn to a speech by Lord Moulton as head of the British Dyestuffs Corporation,[2] and to Mr. Milton Sharp's speech as chairman of the Bradford Dyers' Association.[3] Correspondence to the *Manchester Guardian* during the last week in November provides a full statement of the case from various points of view. The difficulty is to reconcile assistance to the British dye makers with the interests of the colour users and of the textile trade as a whole. There is distinct danger that the textile trade may suffer through difficulty in getting dyestuffs which have special properties. Past experience of a Government Department in the issuing of licences has not inspired dyers with confidence that things will work smoothly under such a system of control. The requirements of one firm differ so much from those of another that a majority vote of colour users cannot settle the point and it is to be anticipated that firms like the Calico Printers' Association or others requiring special dyestuffs will have difficulty in making their claims good in all cases. At the best there is sure to be delay which will be prejudicial to the smooth working of the industry.

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[1] *J.*, 1920, 67T.

[2] *J. Soc. Dyers & Col.*, 1920, **36**, 29.

[3] *Ibid.*, 120.

Considerable attention has been directed during the last twelve months to the use of cellulose acetate produced by the British Cellulose Co. by the Dreyfus process. This product was used during the war as a dope for aeroplanes, and an outlet has been sought in the production of artificial silk. One of the main difficulties in the way of its successful employment in this way has been the problem of dyeing it satisfactorily. Reference to this point was made in an article by L. P. Wilson,[4] to which J. F. Briggs replied,[5] without disclosing the means by which the dyeing of the fibre had been satisfactorily carried out. Cellulose acetate silk cannot be dyed by direct cotton colours without preliminary treatment. Its lack of affinity for colouring matter seems to be associated with the replacement of the hydroxyl groups of the cellulose by acetyl groups. The presence of hydroxyl in many cases determines the affinity of a material for dyestuffs. For example, if cotton goods are mordanted with silicic acid preparatory to dyeing with basic colours,[6] it is found that the affinity for dyestuffs is much diminished if the goods are thoroughly dried before dyeing. Many of the known methods of treating cellulose acetate silk preparatory to dyeing appear to involve a kind of hydrolysis which may be complete for a portion of the fibre or partial throughout the fibre. According to a process of Knoll u. Co., however, in which the silk is caused to swell by treatment with dilute inorganic acids, the inventors claim that there is no actual hydrolysis of the silk substance. Other materials which have been suggested for preparing the silk for dyeing[7] are a mixture 50 % alcohol and 30 % acetic acid, followed by dyeing with basic dyes and 1 % of sodium phosphate; or a mixture of alcohol, acetic acid, and acetone may be used. Basic dyes in alcohol only or in water only do not dye the fibre, but in a mixture of alcohol and water dyeing occurs. Various substances which may subsequently be developed into dyes are absorbed by a fibre directly from aqueous solution. All these processes involve considerable complexity of treatment as compared with that necessary for the dyeing of viscose. Nevertheless, the British Cellulose product possesses certain properties which distinguish it for technical use from viscose. The fact that it does not dye, that it will withstand short treatment in a mercerising solution, and other special features make it seem probable that when the acetate silk has received further technical attention it may find an extensive use in ways in which it does not come into direct competition with viscose. Such use can only be devised by the joint efforts of dyers and designers of fabrics who work in collaboration.

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[4] *J.*, 1920, 266R.

[5] *J.*, 1920, 286R.

[6] B. Leech, E.P. 29,479, 1913; *J.*, 1915, 135

[7] F.P. 383,636; *J.*, 1908, 332.

C. G. Schwalbe,[8] in an investigation of hydro- and oxycelluloses, found that these substances are converted into a mucilage by mechanical means, more particularly by pressure. The mucilage is converted into irreversible colloid on drying and loses the property of swelling in an atmosphere saturated with water vapour. The mucilage is characterised by very high affinity for mordant bases. In a solution of aluminium sulphate, for example, the base is entirely removed by the mucilage, leaving free acid in the liquor. Neutral salts such as magnesium chloride are similarly affected. The formation of small amounts of such mucilage in mechanical processes during dyeing and printing is possible, and the author suggests that the favourable results obtained in dyeing on the jigger or padding machine are to be attributed to small quantities of oxycellulose which are converted into mucilage by the pressure between the rollers. Other instances frequently occur in dyehouse practice in which some of the results described by the author may be accidentally produced.

SPECIAL TREATMENT OF TEXTILE MATERIALS.

Messrs. Gillet et fils have taken out a number of patents in connexion with the treatment of vegetable fibres by nitric acid. According to one process,[9] raw, bleached, or mercerised vegetable fibres are treated with solutions of cellulose in nitric acid for not less than half an hour without tension and then washed; according to a second process,[10] a solution of starch in 65% nitric acid is employed for the treatment of fabrics, followed by treatment with a solution of any suitable salt to aid the precipitation of the nitrated product, and according to a third patent[11] vegetable fibres themselves are immersed in nitric acid (65–75%) and then washed with water. It is claimed that by these means wool-like properties are conferred on the vegetable material. Printing effects can be obtained by local application of the same processes. An elaborate process for obtaining lustre on cotton yarn or cloth is described in a patent of S. Kashitani[12]; the material is treated in sulphuric acid (sp. gr. 1·56—1·71), washed in water under vibration to remove loose fibres, immersed in a solution of caustic soda, and then treated with a 3% solution of borax. Other new processes for treating yarns or fabrics will be found in the section on "Finishing."

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[8] *Z. angew. Chem.*, 1919, **32**, 355; *J.*, 1920, 58A.

[9] E.P. 136,568; *J.*, 1920, 513A.

[10] E.P. 144,204; *J.*, 1920, 542A.

[11] E.P. 136,569; *J.*, 1920, 654A.

[12] E.P. 144,083; *J.*, 1920, 542A.

P. Krais[13] publishes further accounts of his researches on the bicarbonate process of retting. He finds that this process enables considerable time to be saved in retting either of nettles or flax as compared with the usual warm-water retting. Treatment with chloroform sterilises the nettles so that retting does not subsequently occur unless the mass is inoculated with a stem of unsterilised nettle or with a culture of bacteria prepared from a retting liquor.

The use of chalk alone produces no acceleration in retting. The addition of sodium sulphite produces a much lighter, almost white flax, but the liquors acquire a very disagreeable odour. The odour is considerably improved by the addition of dextrose to the bicarbonate retting liquor. A large-scale trial using 1000 kg. of raw flax, proved the process to be very satisfactory on the big scale. Retting was complete in 42 hours, the liquors were free from offensive smell, and the product was superior to the warm-water-retted material obtained in the same works.

A prize of twenty thousand marks is offered by the Verband Deutscher Leinen-Industrieller e. V., Berlin-Bielfeld, for a method of ascertaining the end-point in the retting of bast fibres, and further prizes for a method of avoiding the objectionable odour and injurious nature of the effluent from the retting process and for a practicable method of drying retted flax and hemp artificially.

An improved method for weighting silk with tin is described in a patent by the Deutsche Gasglühlicht A.-G.[14]; the fibre is saturated with tin chloride, centrifuged, dried at a low temperature, and treated with an alkaline gas, *e.g.*, ammonia. It is claimed that the whole of the tin is fixed as hydroxide, the weighting obtained 2½ times that usually obtained, and the rinsing baths are clear and without precipitate. This appears to be a very valuable process since it saves the loss of tin in the first wash water, the whole of the tin being fixed by the gas before washing. The conditions of "drying at low temperature," it is surmised, must be very carefully controlled to avoid tendering.

The use of a number of products for increasing the strength and elasticity of silk or preventing the tendering of weighted silk is claimed by J. Korselt.[15] The intention appears to be to saturate the silk with materials that are more readily oxidised than the silk fibroin. Suitable substances mentioned are tropine, methylphenmorpholine, pimelic acid, polypeptides, peptones, tryptophane, quinine, etc. It is also claimed that these compounds make the handle of the silk more supple.

[13] *Z. angew. Chem.*, 1919, **32**, 326; 1920, **33**, 102; *J.*, 1920, 11A, 443A.

[14] E.P. 116,102; *J.*, 1920, 17A.

[15] E.P. 136,578; *J.*, 1920, 186A.

[16] U.S.P. 1,343,138-9; *J.*, 1920, 542A.

MERCERISING.

In the mercerisation of cotton fabrics containing viscose silk, injury to the latter is said to be prevened by the addition of formaldehyde, phenol,[16] glycerin, or monoacetin[17] to the caustic soda.

SCOURING PROCESSES ETC.

Considerable progress has been made in the degreasing of wool with volatile solvents. An excellent paper on the subject is published by H. Hey.[18] Amongst the solvents which have been proposed, petrol has been found to have the most advantages. It has been found necessary to arrange that the whole of the grease is not removed, but a regulated amount is left in the material. The solvents, unlike aqueous solutions, do not penetrate the cells of the fibres but remove the grease from the surface in a state of pure solution. Other insoluble substances are then more easily removed by mechanical treatment. The disadvantages attached to the use of soap and alkalis are avoided. By this process wool is left in a better condition for carbonising and there is less risk of damage to the fibre. To economise the solvent successive treatments by small volumes are preferred to treatment by a larger volume in one operation; this affords a means of determining the amount of soluble matter which shall be left on the material. The portions of solvents which contain smaller amounts of soluble matter are used for the first treatment of the next lot of wool material. The author points out that by degreasing wool instead of fleece washing and scouring, the weight of the raw wool would be reduced to 20–40% or more, with a corresponding reduction in the cost of carriage and with greater certainty that the wool would arrive in an undamaged condition for manufacture.

A method for cleansing wool by means of oils such as kerosene, olive oil, anthracene oil, fatty acids, etc., is described by T. Hollis and A. Woodmansey.[19] The oil is circulated at a low temperature through the material until impurities are extracted and only the clean extraction medium is left on the wool. This oil is then removed by means of soluble oil and treatment in water.

A. Pinagel and Aachener Chem. Werke [20] have patented the use of alkaline saponin and an alcoholic fulling oil for treatment of woollen material containing mineral oil.

L. Rinoldi,[21] after drawing attention to the fact that better results are obtained when wool is washed in a bath which has been used for previous lots, makes the suggestion that this improvement in the used bath is attributable to the presence of albuminoid substance in the bath removed from the first batch of wool. The author describes experiments dealing with the cleansing of raw wool with baths containing glue. It is found that there is 4–5% less loss of weight and that the wool is softer and better. The use of baths containing 2–3 parts of glue for 1–2 parts of soap is recommended. In preparing garments for re-dyeing the garment is steeped in a warm 4–5% solution of glue without other addition, after which the garments are cleansed by working in water only. The addition of glue to the dye bath is found to assist the penetration and levelling qualities of acid and mordant colours.

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[17] U.S.P. 1,346,802-3; *J.*, 1920, 595A.

[18] *J. Soc. Dyers & Col.*, 1920, **36**, 11; *J.*, 1920, 185A.

[19] E.P. 137,747; *J.*, 1920, 360A.

[20] G.P. 314,403; *J.*, 1920, 154A.

[21] *Prog. Ind. Tint. Tess.*, **19**, 18.

S. Begg[22] describes in a very practical way the scouring and milling of fancy woollen piece goods; the paper contains statistical details comparing soap milling with acid milling and the output of different types of machines. The practical details of the operations are very effectively described in considerable detail.

F. Bayer u. Co.[23] patented a method for de-gumming silk by means of water under pressure. The silk is treated for half-an-hour with distilled water containing 0·25% of caustic soda under pressure of ½ atm. The novelty in this patent appears to be not the use of pressure, but the absence of soap.

BLEACHING.

No new bleaching agent has come into general use nor has there been any striking modification of existing processes.

The bleeding of indigo-dyed threads during bleaching is the subject of a note by R. Aue.[24] The author attributes the bleeding to the reducing action of the dressings in the material in conjunction with the alkali during the scouring. Satisfactory results are obtained by the addition of sodium peroxide (1¼ kg. in 2000 l.) and boiling at a pressure of 0·3 atm.

For the bleaching of paper yarns and fabrics F. E. Jagenberg[25] suggests a preliminary treatment in a solution of hydrosulphite, rinsing, chlorination for six hours, and souring with a solution of sulphuric and hydrochloric acids, followed by thorough rinsing with sodium carbonate and finally with water. The treatment is repeated and is said to yield a pure white without affecting the strength.

THEORY OF DYEING.

In connexion with the general theory of dyeing there is little to report. An investigation of the action of salts on the dyeing of cellulose with benzopurpurin by J. Boëseken and others[26] shows that the action is similar to the salting out of soaps. The necessary quantity of electrolyte is considerably greater than equimolecular. In the case of sulphates and chlorides the strongest electropositive metals exert the most powerful action. Except at high concentration the quantity of dye fixed on the fibre is, within certain limits, proportional to the concentration of the electrolytes and not to the concentration of the dye.

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[22] *J. Soc. Dyers & Col.*, 1920, **36**, 38; *J.*, 1920, 483A.
[23] G.P. 301,255; *J.*, 1920, 13A.
[24] *Bull. Soc. Ind. Mulhouse*, 1919, **85**, 44; *J.*, 1920, 104A.
[25] G.P. 299,651; *J.*, 1920, 400A.

DYEING PROCESSES.

The year is characterised by the absence of new colouring matters, but considerable attention has been paid to refining the methods of application of existing materials.

A new way of dry-dyeing in a bath of carbon tetrachloride is patented by V. Planté.[27] The apparatus used consists of an iron vat containing an iron wire basket in which the material to be dyed is placed, and fitted with connexions for an electric current. The solvent used is a mixture of carbon tetrachloride and alcohol to which is added a mordant of ammonium gallotrioleate in addition to the dye. The colour is fixed on the fibre by means of the electric current.

The use of the colouring matter in plants for dyeing purposes has been investigated by A. E. Everest.[28] The anthocyan pigments give rich shades which are fast to light but not fast to washing. These glucosides yield anthocyanidins on hydrolysis and both these classes of compound dye full shades on tannin-mordanted cotton. The glucosides have scarcely any dyeing affinity for mordanted wool, but the corresponding anthocyanidins dye readily. The affinity for tannin-mordanted cotton is shown by the author to be due to the presence of the pyrylium ring. The chief drawback to the technical use of these colouring matters is their lack of fastness to washing, even to hot water, and their extreme sensitiveness to acids and alkalis. The author describes researches which have been made into the group of related synthetic compounds, which have not, however, at present yielded dyes of technical importance.

In connexion with the production of inorganic colours on the fibre, J. Barnes and others[29] describe the control of the shades produced by mixtures of titanium and iron salts by adjustment of the degree of acidity or basicity of the solution. The effect of the iron is reduced by increased acidity. V. H. Gatty[30] describes the use of a mixture of copper and manganese; the fabrics are padded with a mixed solution of salts of these metals and then passed through a hot alkaline bath.

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[26] *Proc. K. Akad. Wetensch.*, 1919, **27**, 614; *cf. J.*, 1919, 497A.

[27] E.P. 119,881; *J.*, 1918, 765A.

[28] *J. Soc. Dyers & Col.*, 1920, **36**, 47; *J.*, 1920, 483A.

[29] E.P 132,345; *J.*, 1919, 898A.

[30] E.P. 133,620; *J.*, 1920, 17A.

The dyeing of Aniline Black is the subject of several sealed notes of the Société Industrielle de Mulhouse. M. Prud'homme[31] describes a process for wool in which the material is mordanted for 5–10 minutes in a bath of 10–20 g. per litre of chromic acid, squeezed lightly, washed, and dried. It is then impregnated in a cold bath containing aniline and an acid, preferably formic acid, squeezed, and aged. The oxidation is complete in about 1–1½ hr. The material is then well washed and dried without further treatment. The use of organic acids prevents too rapid oxidation of the aniline in the bath. The use of a concentrated bath is advantageous. In a second note Prud'homme[32] recommends addition of a ferric salt to the above mordanting bath.

Other references to Aniline Black will be found under the section on "Printing."

The dyeing of paper yarns is a problem which has received some attention. The addition of oxidising agents such as sodium perborate and percarbonate to the dye-bath is recommended by Chem. Fabr. Coswig-Anhalt.[33] The substance is in this way rendered more easily impregnated, becomes softer to the touch, and brighter colours are obtained. Additional assistants to the dye-bath with substantive colours are boric acid, acetic acid, ammonium chloride, ammonium phosphate.[34]

E. Püschel[35] describes the dyeing of pulp destined to be used for preparing textile yarns. The resin size is added first, then the dyestuff, and finally the aluminium sulphate after half-an-hour's mixing. No mordant is needed with mineral, basic, or acid colours. With acid colours 5% of size gives the best result. If substantive colours are used the pulp should be made neutral or faintly alkaline with soda ash.

In connexion with foam dyeing the use of sulphonic acids of xylene and solvent naphtha to promote the production of a foam has been patented by Meister, Lucius, u. Brüning.[36]

Under the research scheme of the Society of Dyers and Colourists a note on black dyeing on tussore silk is published by J. P. Srivastava.[37] The author was at some pains to obtain samples of genuine reeled tussore unmixed with other varieties of wild silks. He has made a large number of experiments in the use of different dyestuffs and finds that the best results are obtained on silk which has been boiled with water only for one hour preparatory to dyeing. The absorption of dyestuffs was in many cases slightly greater by silk treated in this way than by silk de-gummed completely with soap or alkalis. This result is interesting but of no immediate technical utility, because, as the silk generally comes into the hands of the dyer after manufacture, the treatment with boiling water only would be insufficient to remove the additions made during the process of manufacture. The generally accepted explanation of the difficulty of producing a good black on tussore is that the furrowed nature of its surface causes a scattering of white light in manner quite different from that occurring at the surface of a true silk. It seems possible that the incomplete removal of the gum in the above experiments has led to this surface-effect being less prominent. As regards the point of absorption, it is known that the absorption of dyestuffs by a silk incompletely de-gummed is greater than by one from which all the gum has been removed.

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[31] *Bull. Soc. Ind. Mulhouse*, 1919, **85**, 39; *J.*, 1920, 104A.

[32] *Ibid.*, 42; *J.*, 1920, 104A.

[33] G.P. 315,311; *J.*, 1920, 186A.

[34] G.P. 310,965; *J.*, 1920, 159A.

[35] *Papier-Zeit.*, 1919, **44**, 1742; *J.*, 1920, 12A.

[36] G.P. 312,867; *J.*, 1920, 17A.

[37] *J. Soc. Dyers & Col.*, 1920, **36**, 173; *J.*, 1920, 514A.

In connexion of grege silk, E. L. Maupai[38] has patented a method of hardening the gum by preliminary immersion in a solution of a metallic salt.

PRINTING.

A novel style is described in a patent[39] granted to the Calico Printers' Association, E. Schofield, and F. Farnworth, according to which colour effects of a variegated nature are produced by applying one colour to the under surface of the cloth, by means of brushes, in such a way as to secure complete penetration, and immediately afterwards allowing a second colour to fall on to the upper surface of the cloth in the form of drops. Mechanical arrangements provide for the regulation of the means of brushing and of the number and size of the drops.

Several papers have been published dealing with Aniline Black in printing. E. Jentsch[40] recommends a method of preparing a padding liquor for "discharge" printing which does not differ markedly from general practice.

A. Scheurer[41] gives the following preparation: Potassium ferricyanide 35 parts, potassium chlorate 35 parts, aniline 65 parts, hydrofluosilicic acid (sp. gr. 1·16) 105 parts, and starch water containing 125 g. per litre 760 parts. No copper, vanadium, or hydrochloric acid is used. The colour is developed into an ungreenable black by suspension in an ager at 45° C. For coloured resists under Aniline Black P. W. Pluzanski[42] recommends a printing paste containing caustic soda and stannous chloride. For blue or yellow, Indanthrene Blue or Flavanthrène is used, or the cloth may be first prepared with β-naphthol and the resists developed with diazo compounds.

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[38] U.S.P. 1,325,015; *J.*, 1920, 687A.

[39] E.P. 139,373; *J.*, 1920, 484A.

[40] *Färber-Zeit.*, 1920, **31**, 75; *J.*, 1920, 400A.

[41] *Bull. Soc. Ind. Mulhouse*, 1919, **85**, 292; *J.*, 1920, 483A.

For printing with basic dyes, A. Stiegler[43] recommendsi the use of lead acetate instead of antimony salts. Lactic acd is added to prevent formation of the lead colour lake in the printing paste.

In connexion with indigo, A. Scheunert and N. Wosnessensky[44] recommend a discharge paste containing zinc oxide and Leucotrope W in addition to the usual caustic soda and glucose. M. Battegay reports very favourably on this process (*loc. cit.*).

For direct printing of indigo blue, L. Caberti, C. Barzaghi, and P. Roggieri[45] recommend a paste containing anhydrous sodium sulphite, ammonium oxalate, and zinc powder. Baumann reports that good results are obtained. Ammonium hydrosulphite is formed by the above compounds in the paste.

The grey produced by indigo by printing with starch and olive oil followed by steaming has been shown by R. Haller[46] to be an optical effect due to the reflection of light by the particles of pigment adhering to the fibre. Graphite adhering in particles to the fibre produces a similar effect.

The discharge of alumina, chrome, and iron mordants which are fixed on the cloth as tannates may be successfully performed with alkaline pastes. A patent has been granted to the Calico Printers' Association for such a process.[47]

FINISHING.

As softening agents in finishing, glycol is suggested by T. Goldschmidt A.-G.,[48] and the use of the amyl ether of β-naphthol for increasing the softness and flexibility of artificial silks has been patented by Bayer u. Co.[49]

In the beetling process the use of a continuous rubber sheet wound on between successive layers of cloth is suggested by J. H. Wrigley and A. B. Henshilwood[50] to avoid the production of water-mark effects and to equalise the effect of beetling on different parts of the cloth. Attention has been drawn to the detrimental effect of the presence of small amounts of oil or grease on beetling, and a patent has been taken out by J. D. Lumsden, W. R. MacKenzie, E. H. Robinson, and M. Fort[51] for a process for removing the grease with dry solvents before beetling.

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[42] *Ibid.*, 1920, **86**, 231; *J.*, 1920, 569A.
[43] *Ibid.*, 173; *J.*, 1920, 686A.
[44] *Ibid.*, 263; *J.*, 1920, 745A.
[45] *Ibid.*, **85**, 46; *J.*, 1920, 104A.
[46] *Kolloid-Zeits.*, 1919, **25**, 49; *J.*, 1919, 897A.
[47] E.P. 145,240; *J.*, 1920, 569A.
[48] G.P. 305,192; *J.*, 1919, 859A.
[49] G.P. 307,125; *J.*, 1920, 400A.
[50] E.P. 137,948; *J.*, 1920, 362A.

A special finish by means of the Schreiner calender is described by J. B. Lomax.[52] The fabrics are passed through a calender under very heavy pressure and at as high a temperature as they will withstand without injury. Immediately on leaving the calender the cloth receives a finishing liquor consisting of a boiling solution of alizarine oil. The cloth is then wound on rollers and allowed to stand for 10–12 hours and is finally stretched and stentered.

As a textile dressing and especially for fixing powders or pigments on textile materials, water-soluble phenol-formaldehyde condensation products are suggested by F. Günther.[53] The addition of a cellulose ester increases the elasticity of the product.

PROOFING.

Fabrics may be proofed against soiling or staining by applying a solution of cellulose nitrate or acetate superficially.[54] The cellulose solution is prevented from soaking into the fabric by first impregnating the latter with a volatile liquid such as benzine.

A fabric made of wool mixed with the silk obtained from the innermost layer of the cocoons was one of the products of the war. It is found to be much more permeable to water than a woollen fabric, and ordinary waterproofing methods do not give satisfactory results. G. Colombo[55] describes a process resembling decatizing which considerably decreases the permeability to water of such fabrics.

Insoluble alginates, formed on fabrics by padding with a soluble alginate and then passing through a bath of zinc sulphate or similar heavy metal salt, separate in colloidal form and give a waterproof finish which resists a boiling neutral dye-bath, according to a patent by E. Naefe.[56]

For rendering balloon fabric impermeable to gases the use of a mixture of rubber and cellulose acetate has been patented by Soc. Anon. Etabl. Hutchinson.[57] This mixture can be applied in the form of a colloidal mixture in such solvents as tetrachloroethane.

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[51] E.P. 137,968; *J.*, 1920, 362A.
[52] E.P. 137,710; *J.*, 1920, 362A.
[53] G.P. 318,509; *J.*, 1920, 445A.
[54] L. J. Cavanaugh, E. P. 133,180.
[55] *Giorn. Chim. Ind. Appl.*, 1920, **2**, 234; *J.*, 1920, 816A.
[56] G.P. 314,969; *J.*, 1920, 264A.
[57] E.P. 129,630; *J.*, 1920, 482A.

ACIDS, ALKALIS, SALTS, ETC.

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As mentioned in last year's report, the war has forced even the politicians to recognise the national importance of a secure supply of fixed nitrogen. Considerable progress has been made during 1920 in providing this; the number of papers dealing with some aspect of the nitrogen-fixation problem is a conspicuous feature of the year's literature, and much has been accomplished which has not yet appeared in print. For example, the researches carried through for the Nitrogen Products Committee, whose final report appeared just too late for notice last year, may be published in full.[1]

A number of German patents, granted during the war, have now become available and throw interesting light on the difficulties which confronted our former enemies and on the means taken to surmount them. The largest group of these patents refers to methods of obtaining sulphur or sulphuric acid from gypsum or magnesium sulphate.

Broadly speaking, technical progress has been hindered by commercial difficulties. The high cost of materials and the scarcity and inefficiency of labour have stopped all but the most essential building operations. The demand for increased working capital, necessitated by high costs, has made it difficult and expensive to finance new ventures; at the same time the prospects of satisfactory financial results have become uncertain owing to the curtailed demand due to high prices (especially from European countries with depreciated currencies) and to the incidence of taxation. It is satisfactory to be able to record that the costs of some of the materials widely used in chemical manufacturing are now diminishing, but it would be premature to say that such fundamental items as fuel, labour, and transport have yet reached their maximum cost.

NITROGEN COMPOUNDS.

The statistics of the world's production of nitrogen compounds up to 1918, given in last year's report, are in substantial agreement with those published subsequently in the final report of the

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[1] *Nitrogen Products Committee, Final Report,* 1920, 70.

Nitrogen Products Committee. Since then no complete statistics have appeared; from the partial figures available it appears that a considerable reduction in output has occurred. The world's production for 1919-1920 is estimated[2] as :—

	Tons.	Tons nitrogen.
Chile nitrate	1,910,000 ..	286,000
By-product ammonium sulphate ..	970,000 ..	196,000
Synthetic products	750,000 ..	150,000
		632,000

This is considerably less than the 1913 output, and only some 60% of that of 1917.

Chile nitrate is still the main source of combined nitrogen; the output, after falling off at the close of the war, is again increasing, the figures, in thousands of tons of nitrogen, being[3] :—1913, 416; 1914, 370; 1915, 264; 1916, 437; 1917, 452; 1918, 426; 1919, 251; 1920, about 350.

The production of by-product ammonia in Great Britain has also recovered its pre-war dimensions: expressed in thousands of tons of nitrogen the quantities made were[4] :—1913, 75; 1914, 73; 1915, 71; 1916, 64; 1917, 62; 1918, 67; 1919, 80. It is of interest that 81% of the British product was used in home agriculture in 1918 as compared with 10% in 1913.

The productive capacity of Germany is (1000 tons N per ann.) estimated to be,[5] Haber ammonia 300, cyanamide 120, by-product ammonia 100; but this is far from being fully utilised.

The French output of calcium cyanamide[6] has increased from 1·5 (1000 tons N) in 1913 to 40 in 1919.

AMMONIA.

The synthesis of ammonia from its elements must occupy a prominent place in any account of progress during the year 1920, since it seems clear that most countries, not abundantly supplied with water power, will ultimately depend on this process for an independent supply of fixed nitrogen. In the United States the government plant at Sheffield, Alabama, was referred to last year. In addition to this the General Chemical Co. has a plant at Laurel Hill, N.Y. This company, together with the Solvay Co., has formed the Atmospheric Nitrogen Corporation with a capital of 5 million dollars to exploit this process. In Great Britain the erection of a plant at Billingham-on-Tees was begun early in 1918 at the instance of the Nitrogen Products Committee.[7] In 1920 this was taken over by Synthetic Ammonia and Nitrates, Ltd., a company with a capital of £5,000,000 formed by Brunner, Mond and Co.[8] Plant for the production of 100 tons of NH_3 per day is to be installed as quickly as possible, and provision made for its extension to three times this output. The large quantity of carbon dioxide obtainable as a by-product in making hydrogen is to be utilised, together with the ammonia, for decomposing salt by the ammonia-soda process, yielding sodium bicarbonate and ammonium chloride, in which form it is hoped to market the ammonia for use as a fertiliser.

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[2] *J.*, 1920, 295R.

[3] Imperial Mineral Resources Bureau; *J.*, 1920, 417R.

[4] *Report of Sulphate of Ammonia Assoc.*, 1919; *J.*, 1920, 44R. *Chief Inspector of Alkali Works, 56th Report*, 1919; *J.*, 1920, 277R.

[5] *J.*, 1920, 59R, 382R.

[6] *J.*, 1920, 182R.

[7] *Nitrogen Products Committee, Final Report*, 1920, 133.

In France, the Société Génerale des Industries de l'Air Liquide et de l'Azote, with 25 million francs capital, has been formed to carry out the Claude process,[9] which is being worked experimentally at Grande Paroisse with an output of 1 to 1·5 tons per day.[10] The rights of the Claude process in this country have been acquired by Cumberland Coal, Power, and Chemicals, Ltd., who intend to erect works to make 50,000 tons of ammonium sulphate per ann. in West Cumberland.[11]

Turning to the technical side of the process, R. O. E. Davis and H. Bryan[12] have published useful details of construction of apparatus suitable for laboratory trials. The mixture of hydrogen and nitrogen under the necessary pressure is obtained by decomposing ammonia obtained from a cylinder of the anhydrous liquid and purifying the products. The synthesis takes place in a nickel-chrome steel bomb containing an alundum tube wound with a nichrome heating coil within which the catalyst is placed.

The patented descriptions of plant for large scale operations which have appeared[13] follow, in general, well known lines—a heated container for the catalyst surrounded by a strong shell to withstand the pressure and heat interchangers for transferring heat from the outgoing to the incoming gases. The value of the modifications of detail proposed could only be judged by the results of practical working.

H. C. Greenwood[14] proposes to increase the efficiency of the heat interchanger by causing one or both of the gases to flow through it with a velocity higher than the critical value.

Two patents of the Badische Co. of rather old date[15] state that steels containing Cr, V, or W are suitable for the outer shell even when they contain carbon because, if the alloying metal is present in sufficient quantity, they retain their strength after the carbon has been removed by the action of the high-pressure hydrogen. Nickel should be avoided unless the other alloying metal is present in considerable quantity ; a steel containing 5% each of nickel and tungsten, for example, is suitable.

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[8] *J.*, 1920, 209R.

[9] *J.*, 1920, 167R.

[10] *J.*, 1920, 381R.

[11] *J.*, 1920, 40R.

[12] *J. Ind. Eng. Chem.*, 1920, **12**, 287, 289; *J.*, 1920, 401A.

[13] L'Air Liquide, E.P. 129,637; *J.*, 1920, 63A. E.P. 142,150; *J.*, 1920, 487A. General Chemical Co., E.P. 124,762; *J.*, 1920, 108A.

[14] U.S.P. 1,329,327; *J.*, 1920, 231A.

[15] G.P. 298,199 (1913) and 306,333 (1916); *J.*, 1920, 656A.

The advantages obtainable by the use of a pressure of 1000 atm. are ably set forth by G. Claude.[16] At the higher pressure both the speed of reaction and the concentration of ammonia obtainable are much increased ; for example at 600°, 6 g. of NH_3 at 25% concentration is produced per gram of catalyst per hour, compared with 0·5 g. of NH_3 at 6% concentration made by the Badische Co.'s process. Owing to this increase the apparatus required for a given output is smaller and therefore less costly, and the smaller joints are more easily made, notwithstanding the greater pressure. The number of passages of the gas over the catalyst is reduced and the loss of heat from the smaller apparatus is less, at the same time the quantity of heat evolved for unit volume is greater, so that the reaction is thermally self-sustaining even in small units. Owing to the higher ammonia concentration and higher pressure the ammonia is easily condensed by cooling alone, without the use of water as an absorbent.

The preparation of a cheap mixture of hydrogen and nitrogen is of first importance in the economics of this process. The proposals which have appeared during the past year are on familiar lines. J. Harger[17] setting out from producer gas of suitable composition converts the greater part of the carbon monoxide into carbon dioxide and hydrogen by treatment with steam in presence of iron oxide. The remaining carbon monoxide is oxidised selectively by means of air and a second catalyst. The carbon dioxide is then absorbed, after compressing the gas, by ammonia and the gas submitted to a final purification with caustic soda.

The General Chemical Co[18] recommend a similar procedure but remove carbon dioxide, after the steam treatment, by washing with water at a pressure not exceeding 1400 lb. per sq. in., the final removal of carbon monoxide being effected with caustic soda followed by cuprous ammonium carbonate. C. Ellis[19] removes the carbon monoxide from a mixture of water-gas and producer-gas by liquefaction.

H. C. Greenwood[20] has patented the use of an alkali metal amide for effecting the final purification of either the hydrogen or the nitrogen; and G. Claude[21] suggests coke-oven gas as a source of hydrogen.

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[16] *Chim. et Ind.*, 1920, **4**, 5 ; *J.*, 1920, 655A. *Comptes rend.*, 1920, **170**, 174 ; *J.*, 1920, 187A. *Comptes rend.*, 1919, **169**, 1039 ; *J.*, 1920, 61A.

[17] E.P. 142,874 ; *J.*, 1920, 516A.

[18] E.P. 120,546 ; *J.*, 1920, 231A.

[19] U.S.P. 1,327,029 ; *J.*, 1920, 231A.

[20] U.S.P. 1,337,903 : *J.*, 1920, 488A.

An elaborate study of those catalysts which do not contain alkali metals and therefore do not require absolutely dry gases has been made by M. Guichard and his collaborators.[22] The life of iron, cobalt, nickel, tungsten, and molybdenum is extended by the addition of a refractory oxide such as magnesia or alumina. Of 400 catalysts examined, the combination Fe-Mo was the most resistant and gave the highest concentration of ammonia. It was best prepared by precipitating ferric nitrate with ammonium molybdate and igniting and reducing the precipitate. Under the same conditions the concentrations obtained were :—Fe-Mo, 4%; Fe, under 1%; Mo, under 1·5%; Ni or Co, 3%. Uranium gives good results in the absence of moisture, but its combinations with other metals are less active.

Other catalysts proposed during the year are palladium-asbestos,[23] mixtures containing salts of cyanamide,[24] and fluid mixtures of finely divided cerium or cerium alloy with paraffin or cottonseed oil.[25]

H. C. Greenwood[26] finds that a high velocity of the gases over the catalyst improves the output of ammonia. Using 1¼ million litres of gas per hour per litre of catalyst space and a pressure of 100 atm., he obtains 15 kg. of NH_3 per hour; the gain in output is obviously compensated by a loss of concentration, which would be under 2% in this case.

When water is used for condensing the ammonia the supply of water may be indicated by means of a flow meter, using an aniline gauge to show the differential pressure, and the strength of the liquor observed continuously by allowing it to flow through an electrolytic cell in which its conductivity is measured.[27]

H. W. Foote and M. A. Hunter[28] have studied the properties of solutions of ammonium thiocyanate in ammonia. The vapour pressures of the saturated solutions are relatively small, increasing from 1 mm. at –78° to 41 mm. at 0° and 225 mm. at 20° C. The solutions contain 23·3% NH_3 at 0° and 22·65% at 20°. By means of ammonium thiocyanate, therefore, 98% of the ammonia can be taken up from the gases at –20°, for example.

E. B. Maxted and T. A. Smith[29] suggest the use of cobaltous chloride, which absorbs ammonia at high pressures and gives it up again at lower ones.

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[21] *Chim. et Ind.*, 1920, **4**, 5; *J.*, 1920, 655A.

[22] *Bull. Soc. d'Encour.*, 1920, **132**, 71; *J.*, 1920, 362A.

[23] L'Air Liquide, E.P. 129,637; *J.*, 1920, 63A.

[24] J. C. Clancy, U.S.P. 1,352,174 and 1,352,178–1,352,182; *J.*, 1920, 688A.

[25] F. J. Metzger, U.S.P. 1,313,314-6; *J.*, 1920, 334A.

[26] U.S.P. 1,312,534; *J.*, 1920, 688A.

[27] E. K. Rideal and A. G. Tarrant, E.P. 143,341; *J.*, 1920, 516A.

[28] *J. Amer. Chem. Soc.*, 1920, **42**, 69; *J.*, 1920, 265A.

[29] E.P. 134,572; *J.*, 1920, 21A.

The final conversion of the ammonia into the chloride by means of the ammonia-soda process, already alluded to, is patented by Société l'Air Liquide.[30]

The synthesis of ammonia by other methods has received comparatively little attention. The patents of M. Shoeld[31] and of G. Herman,[32] for making aluminium nitride, may be mentioned here: processes utilising cyanides are dealt with below.

AMMONIUM SALTS.

J. R. Partington and G. J. Jones[33] find that ammonia gas and nitric acid vapour combine to a mist which can be dried by passage through concentrated sulphuric acid with very little loss, after which it is readily condensed. Ammonium nitrate may also be synthesised directly from nitric oxide and ammonia by mixing them with excess of oxygen and with a quantity of steam equivalent to the ammonia. With gases containing 10% of nitric oxide, for example, from 3 to 4 times the theoretical quantity of oxygen is needed.

Ammonium nitrate melts at 169·6° C., and its three changes of state occur at 32·1°, 84·2°, and 125·2° respectively.[34] The melting point of ammonium sulphate in a sealed tube is 417°–423°; in an open vessel the acid sulphate produced, of course, melts more easily, at 336°–339°, according to C. Caspar.[35]

The recovery of by-product ammonia is referred to in the section on Gas (p. 55).

CYANIDES.

The synthesis of sodium cyanide from sodium carbonate, carbon, and nitrogen in presence of iron continues to attract a good deal of attention. J. B. Ferguson and P. D. V. Manning[36] have proved that the reaction $Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO$ is reversible; mixtures of either sodium carbonate or sodium cyanide and carbon when heated in a gas containing carbon monoxide and nitrogen yields the same equilibrium mixture of cyanide and carbonate, the quantity of cyanide present increasing with the temperature and decreasing with the percentage of carbon monoxide in the gas. In producer-gas, for example, containing about 35% CO, a satisfactory degree of cyanisation can only be obtained by working at a temperature approaching 1000° C.

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[30] E.P. 130,365; *J.*, 1919, 690A. F.P. 131,870; *J.*, 1920, 263A.

[31] U.S.P. 1,344,153; *J.*, 1920, 570A.

[32] G.P. 319,046; *J.*, 1920, 570A.

[33] E.P. 134,562 and 136,190; *J.*, 1920, 263A.

[34] R. G. Early and T. M. Lowry, *Chem. Soc. Trans.*, 1919, **115**, 1387; *J.*, 1920, 105A.

[35] C. Caspar, *Ber.*, 1920, **53**, 821; *J.*, 1920, 485A.

[36] *J. Ind. Eng. Chem.*, 1919, **11**, 946; *J.*, 1920, 17A.

On a large scale it is usually proposed to feed briquettes of the carbon-soda-iron mixture through a heated retort in a current of nitrogen. Difficulties arise because (1) the briquettes become plastic and adhere to each other and to the walls of the retort, (2) large quantities of alkali vaporise, and (3) ferrocyanide is formed when the product is extracted with water. Several methods of avoiding one or other of these difficulties have been proposed. E. R. Lewis[37] adds inert, non-alkaline material in sufficient amount to prevent the mass becoming viscid. H. B. Kipper[38] uses an inclined rotating retort. A. Kaufmann[39] adds some carbonised material of high porosity to prevent fusion. W. D. Mount[40] provides mechanical means, at the bottom of the retort, for breaking the solidified mass into fragments. G. Calvert[41] uses enough carbon to prevent the mass sticking together and also proposes mechanical stirring in the retort.

C. P. Hidden[42] avoids vaporisation of cyanide by preheating the charge, as it travels down the retort, to a temperature at which little cyanide is formed; the temperature is then raised suddenly by a blast of hot nitrogen and the cyanide so produced rapidly cooled by a blast of cold nitrogen.

The formation of ferrocyanide during lixiviation is avoided by F. J. Metzger[43] by using a very small quantity of iron in the original charge or[44] by extracting the cyanised product with a mixture of water and an organic solvent, which also prevents hydrolysis of the cyanide.

The production of ammonia from cyanides has been investigated by G. W. Heise and H. E. Foote.[45] They find that alkali cyanides give a good yield of ammonia with steam at 50 lb. pressure and a quantitative yield at 200 lb. Ferrocyanides, on the other hand, gave a maximum yield of 46% in 4¾ hours with steam at 300–330 lb. Cyanised briquettes containing iron yield 90% of their nitrogen as ammonia in 30–45 minutes with steam at 300–330 lb., but at lower pressures higher temperatures (600° at 1 atm.) are required.

E. Briner and A. Baerfuss[46] record the interesting observation that the yield of hydrocyanic acid from a mixture of nitrogen and methane when passed through a high tension arc between platinum electrodes is much increased by lowering the pressure of the gases from 1 atm. to 100 mm.

[37] U.S.P. 1,321,459; *J.*, 1920, 22A.

[38] U.S.P. 1,322,026; *J.*, 1920, 22A.

[39] U.S.P. 1,339,706; *J.*, 1920, 489A.

[40] U.S.P. 1,329,721-2; *J.*, 1920, 232A.

[41] E.P. 140,484; *J.*, 1920, 404A.

[42] U.S.P. 1,352,192-3; *J.*, 1920, 688A.

[43] U.S.P. 1,322,195; *J.*, 1920, 109A.

[44] U.S.P. 1,337,019; *J.*, 1920, 404A.

[45] *J. Ind. Eng. Chem.*, 1920, **12**, 331; *J.*, 1920, 362A.

[46] *Helv. Chim. Acta.*, 1919, **2**, 663; *cf. J.*, 1920, 105A.

The conversion of calcium cyanamide into cyanide by fusion with salt is the subject of a very interesting paper by W. S. Landis.[47] The mixture, of less than one part salt to 2 parts cyanamide and a little calcium carbide, is heated rapidly in a single-phase, electric shaft-furnace with a conducting hearth and a suspended electrode. The temperature used is much higher than was previously considered desirable (about 900°) and the fused product is run off continuously and cooled very rapidly by a water-cooled rotating drum, as it is found that the cyanide disappears on slow cooling. The exact nature of the change does not appear to be known. The product probably contains both sodium and calcium cyanides.

E. Söderbäck[48] has succeeded in preparing free thiocyanogen by the action of bromine on dry lead thiocyanate suspended in dry ether at 0° C. It forms colourless crystals, melting at –3° to –2° and decomposing at the ordinary temperature.

T. S. Price and S. J. Green[49] describe the preparation of cyanogen chloride, on a large experimental scale, from hydrocyanic acid and chlorine. The symptoms of cyanogen chloride poisoning are reported by C. I. Reed[50] to be the same as those of hydrocyanic acid poisoning.

CALCIUM CYANAMIDE.

There is but little to report under this heading. The patents of M. Novak[51] describe a continuous process of manufacture which is very similar to that referred to in last year's report.

A prize offered by the Prussian Ministry of Agriculture for methods of making non-dusty calcium cyanamide produced about 100 suggestions, none of which was entirely satisfactory.[52] The best method is to add 3–4% of heavy tar oil.

NITRIC ACID.

The plant used at H. M. Factory, Craigleith, for the oxidation of ammonia to oxides of nitrogen is described by J. Walker.[53] The mixture of air and (by-product) ammonia, containing from 10–12% NH_3, was filtered through glass- or slag-wool to remove iron oxide particles and then passed, by aluminium tubes, into an aluminium box, 30 cm. side, across which from one to three layers of platinum gauze were stretched horizontally. The gauze had 32 wires per cm., each 0·06 mm. diameter. After activation of the gauze the reaction was initiated by heating a part of the gauze with a flame. The

[47] *Chem. and Met. Eng.*, 1920, **22**, 265 ; *J.*, 1920, 265A.

[48] *Annalen*, 1919, 419, 217 ; *J.* 1920, 189A.

[49] *J.*, 1920, 98T.

[50] *J. Pharm. Exp. Ther.*, 1920, **15**, 301 ; *J.*, 1920, 671A.

[51] G.P. 305,061 and 305,532 ; *J.*, 1920, 488A.

[52] *J.*, 1920, 360R.

[53] *Chem. Soc. Trans.*, 1920, **117**, 382.

temperature of the gauze was 650°–700° C. and the gases left the apparatus at 400°. The time of contact with a single gauze was about 0·001 sec.

The most economical arrangement, according to G. A. Perley,[54] is obtained by using gauze with 120 to 150 wires of 0·0025 in. diam. per inch. Three thimble-shaped gauzes are arranged so that the gas passes them in succession with a rising temperature. The highest velocity of reaction is only attained with preheated gas. G. B. Taylor[55] also finds that the heat of reaction is not sufficient to maintain the optimum temperature of the gauze, which he estimates at 800°; the deficiency can be supplied by enriching with oxygen, by heating the gauze electrically, or by preheating the gases.

B. Neumann and H. Rose[56] find that the best yield of nitric oxide is obtained at a considerably lower temperature; with platinum at 500° (96%); ferric oxide at 670° (96%); iron-bismuth oxides at 600° (95%).

C. L. Parsons and L. C. Jones[57] remove phosphine, the poisonous action of which was described in last year's report, by passing the gases at 50°–60° C. over charcoal, impregnated with a metal of the silver group reduced by hydrogen. The phosphine is oxidised to ammonium phosphate which is easily washed out of the catalyst. F. Bayer u. Co.[58] state that the addition of 2–6% of steam to the mixture of gases increases both the yield and the output of nitric oxide.

Several catalysts are proposed; finely divided silver[59] is said to act at temperatures below 500° C.; nickel gauze coated with nickel oxide,[60] and permutites in which aluminium is replaced by a metal the oxide of which is soluble in alkalis or the alkali by a heavy metal[61] are also mentioned.

Arc process.—F. Gros[62] points out again that a 50% better yield of nitric oxide can be obtained in this process by using a dry mixture of equal volumes of nitrogen and oxygen instead of moist air. He proposes to condense the oxides by cooling and to re-circulate the gases; the heat in the gases leaving the furnace is sufficient to work the plants for refrigeration and oxygen making. C. P. Steinmetz[63] contributes a theoretical study of the process.

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[54] *Chem. and Met. Eng.*, 1920, **22**, 125; *J.*, 1920, 187A.

[55] *J. Ind. Eng. Chem.*, 1919, **11**, 1121; *J.*, 1920, 61A.

[56] *Z. angew. Chem.*, 1920, **33**, 41; *J.*, 1920, 264A.

[57] E.P. 136,342; *J.*, 1920, 108A.

[58] G.P. 299,643; *J.*, 1920, 64A.

[59] W. Manchot and J. Haas, G.P. 300,651; *J.*, 1920, 190A.

[60] H. E. F. Goold-Adams, J. R. Partington, and E. K. Rideal, E.P. 135,224; *J.*, 1920, 62A.

[61] Permutit A.-G., G.P. 298,981; *J.*, 1920, 688A.

[62] *Comptes rend.*, 1920, **170**, 811; *J.*, 1920, 231A.

[63] *Chem. and Met. Eng.*, 1920, **22**, 299; *J.*, 1920, 231A.

Häusser process.—An account of the experiments which had been made with this process up to 1914 is given in Appendix V. to the final report of the Nitrogen Products Committee. The combination of nitrogen and oxygen is brought about by the heat generated by the explosion of a mixture of gas and air. During 1920 patents have appeared, granted to H. Nöh,[64] H. Woll,[65] and J. Görlinger,[66] for modifications in the construction or working of gas engines designed to increase the nitric oxide contents of the exhaust gases.

E. Herman[67] proposes to use flameless combustion at the surface of a mass of aluminium nitride. Methane, burned in this way at 10 atm. pressure, for example, is said to yield 380–490 g. of HNO_3 per cb. m., compared with about 125 g. obtained from coke-oven gas by the explosion method.

Absorption of oxides of nitrogen.—E. K. Rideal[68] has investigated the rate of absorption of nitrogen peroxide by water or nitric acid at temperatures between 30° and 50° C. The rate is proportional to the partial pressure of the NO_2 in the gas when water or dilute nitric acid is the absorbing medium, but it becomes proportional to the concentration of N_2O_4 when stronger acid is used (say 50%). The rate of absorption in water is greater at higher temperatures, but with stronger nitric acid absorption is slower at high temperatures; the inversion takes place at 10% HNO_3.

The limitation of the strength of acid obtainable in absorption towers to 64% HNO_3 is explained thus:—The primary reaction with water is $N_2O_4 + H_2O = HNO_2 + HNO_3$. In presence of nitric acid, nitrous acid decomposes into its anhydride, $2HNO_2 = N_2O_3 + H_2O$; part of the anhydride vaporises and part of it remains dissolved; it is oxidised by oxygen slowly in the gas phase and possibly more rapidly in solution. In addition to this oxidation the reversible reaction $N_2O_3 + 2HNO_3 = 2N_2O_4 + H_2O$ occurs. In the liquid phase at ordinary temperature the molecular ratio N_2O_4 to N_2O_3 is shown to be, in 68% HNO_3, 10·55; in 66·7% HNO_3, 8·51; and in 58·6% HNO_3, 7·17.

Nitric acid containing more than 64% HNO_3 can be produced if the nitrogen trioxide is continuously oxidised by agitation with oxygen, or by refrigeration of a gaseous mixture containing suitable proportions of nitrogen dioxide, water vapour, and oxygen.[69]

E. Wourtzel[70] has redetermined the dissociation constant of N_2O_4

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[64] G.P. 306,451; *J.*, 1920, 404A.

[65] G.P. 316,677; *J.*, 1920, 404A.

[66] G.P. 316,253; *J.*, 1920, 447A.

[67] G.P. 305,124; *J.*, 1920, 404A.

[68] *J. Ind. Eng. Chem.*, 1920, **12**, 531; *J.*, 1920, 514A.

[69] See also F. Foerster, T. Burchardt, and L. Fricke, *Z. angew. Chem.*, 1920, **33**, 113; *J.*, 1920, 484A.

[70] *Comptes rend.*, 1919, **169**, 1397; *J.*, 1920 154A.

between 0° and 85·5°; it can be expressed by $\log K/T = 8{\cdot}9908 - 2810{\cdot}5/T$, from which the heat of polymerisation is 12,850 cals. G. Baume and M. Robert[71] have measured the vapour pressures of mixtures of N_2O_4 and N_2O_3; the boiling point of pure N_2O_3 is calculated from the diagram to be −27° at 760 mm.

J. Walker[72] and M. Kaltenbach[73] describe the usual method of converting nitric oxide, made from ammonia, into nitric acid. The gases are first cooled to 30° C. and then passed up acid-resisting towers (0·9 m. diam. and 5 m. high at H.M. Factory, Craigleith) fed with dilute nitric acid at first. The acid from one tower is elevated by Pohle air lifts, to the top of the next; the finally unabsorbed oxides are caught by milk of lime. The main product is 60% nitric acid.

Instead of absorbing the nitrous gases with water they may be condensed by cooling. P. A. Guye[74] suggests condensing a mixture of N_2O_3 and N_2O_4 which freezes below 0° C. or scrubbing out the N_2O_4 at −20° by a solvent which does not react with it. Similar proposals are made by the General Chemical Co.,[75] E. Thomson,[76] The General Electric Co.,[77] and J. L. La Cour.[78]

The denitration of sulphuric acid is described by J. Walker.[79] The waste acid, containing 69·8% H_2SO_4 and 5·34% inorganic nitrogen calculated as HNO_3, is fed into a square tower of acid-resisting brick divided into six compartments by finely-perforated earthenware plates each of which has a wide overflow pipe sealed in the acid on the plate below. Steam is passed upwards through the tower, no air being used. The outflowing acid contains 66·3% H_2SO_4 and less than 0·1% HNO_3. The dilute nitric acid distilling off is condensed in silica spirals; the gases leaving these are mixed with air and go to oxidation towers to recover the nitrous gases. 93% of the inorganic nitrogen in the waste acid is recovered.

The concentration of dilute nitric acid is carried out in a very similar way, the dilute acid being fed into the top of the tower together with hot concentrated sulphuric acid. According to different patentees the tower may be worked with a current of air or of air and steam, or with neither.[80] It is claimed that 95 to 99·5% acid is obtained.

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[71] *Comptes rend.*, 1919, **169**, 968; *J.*, 1920, 61A.

[72] *Chem. Soc. Trans.*, 1920, **117**, 382.

[73] *Chim. et. Ind.*, 1920, **4**, 576; *J.*, 1920, 655A.

[74] U.S.P. 1,331,104-5; *J.*, 1920, 294A.

[75] E.P. 124,759; *J.*, 1920, 748A.

[76] U.S.P. 1,337,106; *J.*, 1920, 404A.

[77] E.P. 150,836; *J.*, 1920, 721A.

[78] U.S.P. 1,348,227; *J.*, 1920, 656A.

[79] *loc. cit.*

[80] General Chemical Co., E.P. 124,759; *J.*, 1920, 748A. F. Bayer u. Co., G.P. 310,081; *J.*, 1920, 404A. G.P. 297,901, 1916; *J.*, 1920, 62A.; G.P. 297,903; *J.*, 1920, 20A. M. Kaltenbach, *Chim. et Ind.*, 1920, **4**, 576; *J.*, 1920, 655A. H. Pauling, G.P. 305,553; *J.*, 1920, 294A.

A. Clemm[81] proposes to treat dry barium nitrate with concentrated sulphuric acid; by filtering off the barium sulphate a mixture of the acids is obtained which does not act on iron, and concentrated nitric acid is produced by distilling this. The barium sulphate is converted into sulphide and redissolved in dilute nitric acid.

Another method is due to the General Electric Co.[82] A solution of oxides of nitrogen in nitric acid, obtained by scrubbing nitrous gases at -40° C., is electrolysed (using dilute sulphuric acid at the cathode) yielding hydrogen and strong nitric acid.

Nitrates.

The melting point of sodium nitrite is 276·9° C.; its aqueous solutions are not oxidised by oxygen at 50 atm. and at 100° even in presence of catalysts,[83] the dry substance is, however, oxidised slowly to sodium nitrate by oxygen at 175 atm. and 395°–530°.[84]

The deposits of potassium nitrate near Prieska, South Africa, referred to last year, have proved to be of no commercial value.[85]

SULPHURIC ACID.

The increase in the production of sulphuric acid during the war s illustrated by the following figures :—

	1000 tons H_2SO_4 produced in		
	France[86]	Italy[87]	Japan[88]
1913	800	—	—
1914	—	678	—
1915	—	—	219
1918	—	835	566
1919	1700	—	580

C. E. Fawsitt[89] has studied the action of sulphuric acid on mild steel under the conditions of transport in steel drums. The action increases as the strength of acid diminishes from 97·4% to 90·9%. There is a sudden diminution of the action at 89%, after which it again increases with dilution. Shaking increases it considerably. The gas evolved produces pressure in the drums, but of a batch of drums filled with the same acid some developed pressure while others did not. No certain means of preventing action was found.

Contact Process.—F. Schwers[90] has investigated an interesting case of poisoning of the platinum catalyst which resulted from the use of sulphuric acid containing 0·001% As_2O_3 for washing the entering gases. He finds that even in this minute concentration the arsenic vaporises to such an extent that at 60°, 8000 cb. m. of gas carries away 0·1 g. of As_2O_3. R. Curtis and F. D. Miles[91] describe a useful method for the working control of the strength of oleum which depends on noting the rise of temperature when equal volumes of oleum and ordinary strong vitriol are mixed. G. Vortmann[92] states that tin oxide is a good catalyst.

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[81] G.P. 303,313 and 304,233; *J.*, 1920, 294A.

[82] E.P. 150,836; *J.*, 1920, 721A.

[83] C. Matignon and G. Marchal, *Comptes rend.*, 1920, **170**, 238; *J.*, 1920, 188A.

[84] C. Matignon and E. Monnet, *ibid.*, 1920, **170**, 180, *J.*, 1920, 187A.

[85] Imp. Min. Resources Bureau; *J.*, 1920, 417R.

[86] *J.*, 1920, 182R.

[87] *J.*, 1920, 204R.

[88] *J.*, 1920, 387R.

[89] *J.*, 1920, 147T.

[90] *J.*, 1920, 33T.

Calcium or Magnesium Sulphate.—A number of patents have become available during the past year, which indicate the methods adopted in Germany during the war to obtain sulphuric acid from these raw materials. These methods may be divided into several groups.

(A) Gypsum is first converted into calcium carbonate and ammonium sulphate by the action of ammonia and carbon dioxide,[94] a process which, according to D. R. H. Wride,[93] proceeds easily and quantitatively. The carbonate mud is apt to be slimy in presence of silica or alumina, but can be easily filtered by vacuum filters of the leaf type.

The ammonium sulphate may be heated with sodium sulphate yielding ammonia and sodium pyrosulphate at 400° C., the latter regenerating sodium sulphate and sulphuric anhydride at higher temperatures,[95] or it may be slowly heated to 250° with iron oxide until the ammonia is expelled, after which the ferric sulphate is decomposed at redness.[96]

(B) A second method depends on converting the calcium sulphate into sulphide from which hydrogen sulphide is obtained which is then burned to sulphur. The reduction is effected by heating with coal in a revolving furnace at 1100°, some 60% of the theoretical yield of sulphide being obtained which is decomposed by boiling with magnesium chloride.[97] Hydrocarbons at 800°–1300° are also proposed as reducing agents.[98] For the combustion of the hydrogen sulphide a Claus kiln is proposed in which bauxite is used as catalyst,[99] a layer 30 cm. thick at 330° being followed by a layer at 200°. The main reaction is said to take place best at 300°; the secondary reaction $2H_2O + 3S = 2H_2S + SO_2$ being very slow at 200°.

Magnesium sulphate becomes available as a raw material for this process if barium sulphide is used as an intermediary.[99] The reactions proposed are :—

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[91] *J.*, 1920, 64T.

[97] G.P. 316,858; *J.*, 1920, 403A.

[93] *Chem. Age*, 1920, 2, 32; *J.*, 1920, 154A

[94] G.P. 299,752; *J.*, 1920, 364A. G.P. 300,724; *J.*, 1920, 364A.

[95] Badische Co., G.P. 298,491; *J.*, 1920, 63A.

[96] B. Dirks, G.P. 301,791; *J.*, 1920, 263A.

[97] *J.*, 1920, 134R.

[98] G.P. 304,231; *J.*, 1920, 364A. G.P. 319,651; *J.*, 1920, 489A.

$$CaSO_4+Ba(SH)_2=Ca(SH)_2+BaSO_4$$
$$MgSO_4+Ba(SH)_2=Mg(SH)_2+BaSO_4$$
$$Mg(SH)_2+H_2O=MgO+2H_2S$$

or $MgCl_2+Ba(SH)_2=BaCl_2+Mg(SH)_2$ and $BaCl_2+MgSO_4=BaSO_4+MgCl_2$.

(c) F. Weeren[100] proposed to heat gypsum with coke and a silicious flux so as to obtain a fluid slag and sulphur. W. Borchers,[101] using sufficient clay to form a neutral silicate and a temperature of 900°–1300°, states that the sulphur is almost entirely liberated in the form of sulphur dioxide.

The formation of sulphur in this process is due to the reaction investigated by J. B. Ferguson,[102] $SO_2 + 2\,CO = 2CO_2 + S$. The attempts of the Badische Company to utilise it in practice are reported to have been unsuccessful.[103] A number of patents are concerned with this reaction.[104] The slag produced in this process can be used as an hydraulic cement. The form of the process in which sulphur dioxide is produced appears to have been used.[105]

(D) Magnesium sulphate heated in a current of hydrogen sulphide yields magnesia and sulphur dioxide or sulphur according to the proportions of the reactants used. Kieserite yields a mixture of potassium sulphide and magnesia.[106] When heated with carbon at 600°–700°, magnesia and sulphur dioxide are produced.[107]

(E) Gypsum when heated to redness in a current of carbon tetrachloride vapour yields chlorides of sulphur which are converted by water into hydrochloric and sulphuric acids.[108]

Attention may be drawn to an account of an electrical precipitation plant for removing sulphuric acid mist from the gases leaving Gaillard towers,[109] and to the suggestion of the Chief Inspector of Alkali Works that this method might be of service for removing dust from gases entering the catalyst chambers of contact plants.[110]

[99] Chem. Fabr. Rhenania and F. Projahn, G.P. 298,844 ; *J.*, 1920, 749A.

[100] F. Beck, G.P. 302,433 ; *J.*, 1920, 365A ; and G.P. 307,041 and 307,042 ; *J.*, 1920, 406A.

[101] G.P. 301,712 ; *J.*, 1920, 335A. Also Badische Co., G.P. 302, 433 ; *J.*, 1920, 365A. G.P. 300,092 ; *J.*, 1920, 64A.

[102] *Ann. Repts.*, 1919, 4, 166.

[103] *J.*, 1920, 134R.

[104] G.P. 300,715 ; *J.*, 1920, 406A. G.P. 305,123 ; *J.*, 1920, 295A. G.P. 301,682, 302,471, 306,312 ; *J.*, 1920, 570A.

[105] O. F. Kaselitz, *Z. angew. Chem.*, 1920, **33**, 49 ; *J.*, 1920, 265A.

[106] Chem. Fabr. Rhenania, G.P. 300,716 ; *J.*, 1920, 109A ; V. Eichenbrecher, G.P. 307,752 ; *J.*, 1920, 406A.

[107] Badische, G.P. 300,762 ; *J.*, 1920, 109A.

[108] P. Jannasch and E. M. Alberts, G.P. 318,221 ; *J.*, 1920, 403A.

[109] A. Delasalle, *Chim. et Ind.*, 1920, **4**, 291 ; *J.*, 1920, 720A.

[110] *56th Report*, 1919 ; *J.*, 1920, 276R.

POTASSIUM SALTS.

The production of potash salts in Germany was 860,000 tons K_2O, of which 620,000 tons was consumed at home[111]; the production in Alsace during 1920 is estimated at 220,000 tons K_2O.[112] From November, 1918 to February, 1920, 23,581 tons of potash salts had been imported into Great Britain from Germany and 37,358 tons from Alsace[113]; about 100,000 tons of the Alsatian crude salts had also been shipped to America.

The extraction of potassium salts from greensand, the potash-bearing constituent of which is glauconite—a hydrated potassium ferric silicate—is the subject of several patents. It is proposed (A) to digest the sand with lime and calcium chloride and water at 200 lb. pressure[114]; (B) to digest 1 part of sand with ½ part of lime and 3 pts. of water at more than 150 lb. pressure[115]; (C) to separate the glauconite and then treat it with sufficient hydrochloric acid to extract all the metals except iron[116]; (D) to heat the sand with ferrous sulphate[117] or with iron pyrites in presence of air[118] in order to convert the aluminium and potassium present into their sulphates; (E) to digest with a solution of a salt such as sodium nitrate under high pressure.[119]

HYDROGEN.

No novel process of manufacturing hydrogen has been proposed during the year. Forms of apparatus for carrying out the steam-iron process are patented by A. R. Griggs,[120] W. J. and W. R. Bates,[121] and by K. Zöller.[122]

E. F. Armstrong and T. P. Hilditch[123] find that the reaction $CO + H_2O = CO_2 + H_2$ is catalysed by copper at 220° with fair speed, whereas iron oxide is only slightly active at 250°. At higher temperatures, however, iron oxide is far the more active catalyst.

The activity of iron, nickel, or cobalt may be increased by treating them with their oxides or salts.[124] For example strongly heated ferric oxide may be mixed with moist iron hydroxide, or iron gauze dipped in a concentrated solution of ferric nitrate and heated to redness.

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[111] *J.*, 1920, 132R.

[112] *J.*, 1920, 132R.

[113] *J.*, 1920, 100R.

[114] T. C. Meadows, M. Hauber, jun., and H. W. Charlton, U.S.P. 1,327,164 *J.*, 1920, 231A.

[115] H. W. Charlton, U.S.P. 1,329,369 ; *J.*, 1920, 231A.

[116] E. Hart, U.S.P. 1,322,900 and 1,323,228 ; *J.*, 1920, 63A.

[117] M. Hauber, jun., U.S.P. 1,323,764 ; *J.*, 1920, 63A.

[118] W. Glaesser, U.S.P. 1,323,464 ; *J.*, 1920, 63A.

[119] A. C. Spencer, U.S.P. 1,344,830 ; *J.*, 1920, 571A ; A. Messerschmitt, U.S.P. 1,344,705 ; *J.*, 1920, 571A.

[120] E.P. 134,901-2 ; *J.*, 1920, 23A. E.P. 142,882 ; *J.*, 1920, 518A.

[121] E.P. 137,674 ; *J.*, 1920, 232A.

[122] G.P. 300,761 ; *J.*, 1920, 335A.

[123] *Proc. Roy. Soc.*, 1920, **A. 97**, 265 ; *J.*, 1920, 446A.

[124] Badische Co., G.P. 300,032 ; *J.*, 1920, 64A.

The conversion of the carbon monoxide into dioxide is, of course, never complete owing to the equilibrium being approached; H. E. F. Goold-Adams and H. C. Greenwood[125] therefore propose to use several catalyst chambers separated by lime containers and so to diminish the quantity of the reverse reaction.

Hydrogen which is inert in catalytic hydrogenation processes may be activated by adding about 2% of air and passing it over hot, finely-divided nickel.[126]

The adsorption of hydrogen by palladium has been studied by J. B. Firth.[127] It appears that between the temperature of boiling liquid air and 0° the hydrogen is condensed on the surface of the metal only; from 0° to 150° surface condensation followed by absorption into the metal takes place and above 150° the latter only.

Rhodium black (prepared by the reduction of sodium rhodium chloride with hydrazine in acid solution) absorbs 206 times its volume of hydrogen at 0°; the spongy metal absorbs very little.[128]

HYDROGEN PEROXIDE.

The reduction of an aqueous solution of oxygen, saturated under pressure, by palladium saturated with hydrogen is recommended as a mode of making hydrogen peroxide.[129]

F. W. Skirrow and E. R. Stein[130] find that the distillation of potassium persulphate with sulphuric acid yields 80% of the theoretical amount of hydrogen peroxide; the sodium salt only gives 9%. The difference is probably due to the greater freedom of the former from catalysts destroying the peroxide. The mechanism of the reaction has been studied by H. Palme.[131] Caro's acid and hydrogen peroxide are first produced by the reactions: $H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$ and $H_2SO_5 + H_2O = H_2O_2 + H_2SO_4$. Both reactions are of the first order and their velocity increases with the concentration of the sulphuric acid. At 50°, the first is 39 times faster than the second. Secondary reactions leading to a loss of active oxygen are probably represented by the equations $H_2S_2O_8 + H_2O_2 = 2H_2SO_5$ and $H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2$.

By evaporating borates or phosphates with concentrated solutions of hydrogen peroxide under reduced pressure perborates containing up to 28·4% of active oxygen and perphosphates with 12–13% are obtained.[132]

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[125] E.P. 137,340; *J.*, 1920, 232A.

[126] Berlin-Anhaltische Maschinenbau A.-G., G.P. 301,364; *J.*, 1920, 722A.

[127] *Chem. Soc. Trans.*, 1920, **117**, 171; *J.*, 1920, 383A.

[128] A. Gutbier and O. Maisch, *Ber.*, 1919, **52**, 2275; *J.*, 1920, 156A.

[129] E. Moritz, E.P. 120,045; *J.*, 1920, 23A.

[130] *Trans. Amer. Electrochem. Soc.*, 1920, 69; *J.*, 1920, 687A.

[131] *Z. anorg. Chem.*, 1920, **112**, 97; *J.*, 1920, 720A.

Several agents are recommended for preserving solutions of hydrogen peroxide; these are:—0·2% of strontium hydroxide, dextrose, or aniline[133]; 0·002% of acetanilide, with 2% of hydrochloric acid or 0·1% of phosphoric acid, boric acid, and amino-compounds generally[134]; complex salts of salicylic acid which are soluble in water with borax or disodium phosphate.[135]

HELIUM.

A committee of Congress (U.S.A.) has now found that the cost of the helium required to fill an air ship exceeds that of the ship.[136] The known supplies are far from unlimited in duration.[137] From J. C. McLennan's lecture[138] to the Chemical Society, which contains an account of the development of the Canadian resources, it seems that the principal value of helium at present is in the production of extremely low temperatures. (*See also pages* 79-80.)

HALOIDS.

Liquid chlorine, the production of which in this country was developed for war purposes, is now used in several commercial processes. Excess of chlorine above that which can be utilised in the manufacture of bleaching powder is converted into very pure hydrochloric acid by direct combination with electrolytic hydrogen.[139] The sterilisation of water for army use is described by J. S. Arthur[140]; after a preliminary treatment with aluminium sulphate and soda, followed by sedimentation and filtration, the water is treated with chlorine, drawn from cylinders of the liquid substance, and finally dechlorinated with sulphur dioxide; 2 minutes' contact with chlorine is sufficient.

A method of liquefying chlorine by dissolving it in carbon tetrachloride and then expelling the gas into a condenser where it liquefies under the pressure developed is patented by C. T. Henderson.[141]

H. D. Gibbs[142] finds that the reaction between chlorine and water at ordinary temperatures is accelerated by charcoal, and the rather vigorous action of chlorine or bromine on lignite, which yields the corresponding acids and a resin containing halogen, has been patented by Consolidierte Alkaliwerke, Westeregeln.[143]

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[132] Aschkenasi, G.P. 316,997 and 318,219; *J.*, 1920, 406A.

[133] M. Sarason, G.P. 318,134-5, 318,220; *J.*, 1920, 406A.

[134] H. R. Jenson, *Pharm. J.*, 1920, **105**, 871; *J.*, 1920, 596A.

[135] A. Queisser, G.P. 321,616; *J.*, 1920, 689A.

[136] *J.*, 1920, 92R.

[137] *J.*, 1920, 288R.

[138] *J.*, 1920, 252R.

[139] *Chief Inspector of Alkali Works, 56th Report*, 1919; *J.*, 1920, 277R.

[140] *J.*, 1920, 412R.

[141] U.S.P. 1,338,654; *J.*, 1920, 449A.

[142] *J. Ind. Eng. Chem.*, 1920, **12**, 538; *J.*, 1920, 515A.

A mixture of bromine and water dissolves much more potassium bromide than water alone; for moderate concentrations about 0·5 mol. of additional potassium bromide is dissolved per mol. of bromine. The limit is not reached in a solution containing 79·5% Br_2, 15·1% KBr, and 5·4% water.[144]

Iodine pentoxide is prepared, with quantitative yield, by the oxidation of iodine with chloric acid in small excess.[145]

SELENIUM.

In the United States 103,694 lb. of selenium was produced in 1918.[146]

ARSENIC.

The United States produced 6323 tons of arsenic trioxide in 1918, the greater part of which was used as a weed killer.[147]

The trioxide is oxidised, at 400°-480°, to the pentoxide by oxygen at 127–180 atm. pressure.[148] E. O. Barstow[149] has patented the preparation of lead arsenate, a valuable insecticide, by precipitating a solution of basic lead acetate with arsenic acid.

Arsenious chloride is produced quantitatively when the trioxide, mixed with one-fifth its weight of carbon, is heated at 200°–260° C. in a current of carbonyl chloride.[150]

PHOSPHORUS.

Statistics of the production of phosphate rock between 1913 and 1917 are published by the U. S. Geological Survey.[151] The world's production, in metric tons, is given as:—1913, 7,141,822; 1915, 3,852,847; 1916, 4,536,079; 1917, 4,100,675; 1918, about 3,800,000.

The production of a concentrated phosphatic fertiliser continues to attract attention. W. H. Waggaman and T. H. Turley[152] find that when a mixture of calcium phosphate, quartz flour, and carbon is heated at about 1500° C. in a reducing atmosphere until a fluid slag is formed, almost the whole of the phosphorus is expelled in the form of the pentoxide. The presence of a little alumina lowers the melting point of the slag and is advantageous. Large-scale experiments were made with briquettes containing 20 parts of phosphate (20–25% clay), 16·6–22 parts of silica, and 4·8–5·6 parts of coke, which were heated by direct contact with flames. As much as 93·3% of the phosphorus was evolved when a properly fused slag was made.

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[143] G.P. 313,875; *J.*, 1920, 20A.

[144] A. F. Joseph, *Chem. Soc. Trans.*, 1920, **117**, 377; *J.*, 1920, 626A.

[145] A. B. Lamb, W. C. Bray, and W. J. Geldard, *J. Amer. Chem. Soc.*, 1920, **12**, 1636; *J.*, 1920, 626A.

[146] *J.*, 1920, 183R.

[147] *J.*, 1920, 183R.

[148] C. Matignon and J. A. Lecanu, *Comptes rend.*, 1920, **170**, 941; *J.*, 1920, 402A.

[149] U.S.P. 1,349,707; *J.*, 1920, 689A.

[150] L. H. Milligan, W. A. Baude, and H. G. Boyd, *J. Ind. Eng. Chem.*, 1920, **12**, 221; *J.*, 1920, 402A.

[151] *J.*, 1920, 168R.

[152] *J. Ind. Eng. Chem.*, 1920, **12**, 646; *J.*, 1920, 595A.

The production of a solution of ammonium phosphate by treating phosphate rock first with sulphuric acid and then with ammonia is patented by Chemische Fabrik Budenheim.[153]

The solubility of ammonium phosphate has been determined by G. H. Buchanan and G. B. Winner[154]; 100 g. of the saturated solution at 30°–90° contains $18{\cdot}0 + 0{\cdot}455t$ g. of the mono-ammonium salt and, at 10°–70°, $36{\cdot}5 + 0{\cdot}213t$ g. of the di-ammonium salt.

Considerable development took place during the war in the Swedish and Japanese phosphorus industries; the former country now produces all the phosphorus required in its match industry,[155] and the same is true of Japan, where production was stimulated by the cessation of imports of Swedish matches; the cost of phosphorus in Japan is reported to be about one shilling per lb.[156]

CARBON.

In 1918 the world's supplies of natural graphite were contributed by Madagascar (35%), Ceylon (27%), Italy (12%), Mexico, Korea and the United States (6 to 8% each), Canada and Spain (2 to 3% each).[157] In 1913 the largest producer was Austria. The Madagascar industry was founded in 1910 and in 1917 the production reached 27,838 tons, containing 80–82% carbon; in 1919, owing to diminished demand, this had fallen to 6000 tons, but the grade was improved to 90% or more.[158] Natural graphite is mainly used for plumbago crucibles, which absorbs 75% of the supply; lubricants 10%, pencils 7%, foundry work 5%, and paints 3%, account for the remainder.[159] Artificial graphite is used for electrodes, lubricants, paints, dry batteries, and boiler-scale preventives.

G. A. Hulett and O. A. Nelson[160] find that graphitic acid, when heated, loses adsorbed water gradually; decomposition begins at 184° C. and explosion occurs at 218°. It is impossible to distinguish between the loss of adsorbed water and that due to decomposition. They assume that graphitic acid is a colloidal oxide of carbon, the composition of which is expressed by C_3O or $C_{11}O_4$, the differences between different samples being due to the size of the scales of which they consist.

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[153] G.P. 313,964; *J.*, 1920, 64A.

[154] *J. Ind. Eng. Chem.*, 1920, **12**, 448; *J.*, 1920, 515A.

[155] *J.*, 1920, 41R.

[156] *J.*, 1920, 273R.

[157] *J.*, 1920, 78R.

[158] *J.*, 1920, 13R and 83R.

[159] *J.*, 1920, 356R.

[160] *Trans. Amer. Electrochem. Soc.*, 1920, 425; *J.*, 1920, 487A.

The absorption of gases by charcoal was used during the war for affording protection from poison gases and some industrial applications of this property are now suggested.

R. M. Winter and H. B. Baker[161] find a considerable increase in the density of sugar charcoal when it is heated for 40 hours at 900° (1·76 to 1·84). This is accompanied by an increase in the absorptive power for sulphur dioxide from 97 to 288 c.c. per gram. H. H. Lowry and G. A. Hulett[162] observe similar differences in the absorptive power; they find that the surface of charcoal varies from 160 to 436 sq. m. per gram. An application of the absorptive power of charcoal to the concentration of dilute sulphur dioxide was mentioned above; the extraction of petrol from natural gas is another, the absorbed hydrocarbon being liberated by steam.[163]

CALCIUM CARBIDE.

Passing through what at one time must have been the beautiful valley of the Romanche last summer, the writer was vividly impressed by the clouds of white smoke which filled the valley for some miles in the neighbourhood of the carbide works and which was scarcely less depressing than the grey pall which hangs over our own industrial towns. Interesting details of the nature and origin of this fume are given by P. Schläpfer.[164] In making 1000 kg. of calcium carbide, 1000 kg. of lime and 600 kg. of coke are used, of which 121 kg. CaO, 60 kg. of coke ash, and 23 kg of coke dust are carried away with the gases. Large furnaces are said to make more dust than small ones, possibly owing to the higher temperature causing greater dissociation of the carbide. According to J. Baumann[165] over-heating and fume are reduced by using the correct size of electrodes. Apparently attempts to collect the dust in coke scrubbers or by water washing have not been successful; a Cottrell precipitation plant might possibly be useful.

According to A. Kiesewalter[166] calcium hydride is formed if lime is fused electrically in a current of hydrogen and the product cooled in this gas.

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[161] *Chem. Soc. Trans.*, 1920, **117**, 319; *J.*, 1920, 363A.

[162] *J. Amer. Chem. Soc.*, 1920, **42**, 1393; *J.*, 1920, 596A.

[163] *J.*, 1920, 414R.

[164] *Z. Elektrochem.*, 1919, **25**, 409; *J.*, 1920, 188A.

[165] *Chem.-Zeit.*, 1920, **44**, 33; *J.*, 1920, 188A.

[166] G.P. 311,987; *J.*, 1920, 406A.

SILICATES.

The applications of sodium silicate depend on the colloidal nature of its solutions; the more alkaline solutions deposit crystalline substances and are therefore useless. J. G. Vail[167] gives a good account of the properties of these solutions. The composition of commercial water glass lies between $2Na_2O : 3SiO_2$ and $Na_2O : 4SiO_2$; it is limited on the one side by crystallisation and on the other by insufficient solubility. Solutions of the more alkaline glass may be concentrated to sp. gr. 1·916 containing 62·5% of total solids and then form a very viscid, tough mass: the more acid material yields a solution of sp. gr. 1·305 containing 34% of solid matter; this solution is an elastic jelly. Any intermediate condition can be realised. The boiling and freezing points of these solutions differ but little from those of water. Their viscosity increases very rapidly when they pass from the sol to the gel condition and the change may be brought about by increased concentration or by decreased temperature or alkalinity. The removal of 10% of water by spreading a sol on cardboard may bring about this sudden increase of viscosity and so give a quickly setting adhesive.

The tensile strength of water-glass cements is high; acid-proof cements are easily obtained with a strength of 1700 lb. per sq. in. and the baked clay-sodium silicate bond used for abrasive wheels has a strength of 2000 lb. per sq. in. F. J. Phillips and E. J. Rose[168] describe the preparation of acidified solutions of water-glass and J. D. Malcolmson[169] shows how the solutions may be diluted with brine without loss of viscosity by stirring so that the silica first precipitated is re-peptised.

The properties of Japanese acid clay—a kind of fuller's earth—are examined by K. Kobayashi.[170] It is an amorphous mixture of hydrated aluminium silicate and silica which adsorbs hydroxyl ions selectively so that solutions of salts after contact with it are acid.

SODA.

Progress during the year is almost exclusively electro-chemical and is reported under that heading.

ALUMINA AND ITS SALTS.

Several methods of preparing aluminium sulphate from clay or slate have been described. The Köslin Paper Works[171] propose to heat clay with sodium bisulphate and barium peroxide at 300°–400° C., which yields a mass from which aluminium sulphate free from iron may be extracted with water. H. Fleissner[172] heats the clay with calcium sulphate ($Al_2O_3 : 2CaSO_4$) at a dull red heat. Calcium metasilicate and basic aluminium sulphate, which can be extracted with dilute sulphuric acid, are produced. K. J. P. Orton and G. W. Robinson[173] heat slate with 3–4 parts of nitre cake to a cherry-red heat. The solution diluted to 150 times the weight of mineral used is heated to 70°–80° to precipitate ferric hydroxide. Alumina is precipitated from the filtrate. J. Morel[174] treats bauxite with sulphur dioxide, air, and steam in a Hargreaves furnace. The aluminium sulphate produced is extracted with water and precipitated with sodium thiosulphate, $Al_2(SO_4)_3 + 3Na_2S_2O_3 = Al_2O_3 + 3SO_2 + 3S + 3\ Na_2SO_4$. The sulphur compounds are re used.

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[167] *J. Ind. Eng. Chem.*, 1919, **11**, 1029; *J.*, 1920, 106A.

[168] E.P. 151,339 and 151,508; *J.*, 1920, 748A.

[169] *J. Ind. Eng. Chem.*, 1920, **12**, 174; *J.*, 1920, 293A.

[170] *J. Chem. Ind. Tokyo*, 1920, **23**, 543; *J.*, 1920, 655A.

[171] G.P. 301,614; *J.*, 1920, 109A.

The process of extracting alumina from labradorite with nitric acid reported upon last year is patented by Norsk A. S. for Elektrokemisk Ind.[175] An alternative method of recovering the alumina is to precipitate it with ammonia at 10–15 atm. pressure and a correspondingly high temperature. The ammonia is regenerated from the filtrate by heating it with finely ground labradorite.[176]

BARIUM SALTS.

E. Terres and K. Brückner[177] find that an aqueous solution of barium sulphide deposits the compound $Ba(SH)(OH),5H_2O$ at all temperatures. Strontium sulphide on the other hand does not give a mixed compound, pure strontia being deposited from the solutions.

H. Langwell[178] has devised a method of obtaining pure, finely-divided barium carbonate, which depends on the fact that fused sodium chloride dissolves twice its weight of barium carbonate. The insoluble impurities are removed from the fusion and the sodium chloride then washed out with water.

LEAD BORATE.

Only two lead borates exist: $PbO,3B_2O_3$, obtained by fusing lead carbonate and boron trioxide and removing the excess of the latter with water, and $Pb(BO_2)_2,H_2O$, obtained by precipitating a lead salt with excess of a concentrated solution of borax.[179]

THORIA.

According to O. N. Berndt[180] when monazite sand is heated for a long time with concentrated sulphuric acid at 250°–300° a crystalline compound $Th(PO_3)_2SO_4$ is formed which is insoluble in dilute acid; the other rare earths form soluble compounds. In a later patent[181] fuming sulphuric acid is specified.

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[172] G.P. 322,844; *J.*, 1920, 722A.

[173] E.P. 139,005; *J.*, 1920, 294A.

[174] E.P. 149,769; *J.*, 1920, 689A.

[175] E.P. 125,578; *J.*, 1920, 108A.

[176] E.P. 134,531; *J.*, 1920, 597A. U.S.P. 1,333,020; *J.*, 1920, 334A.

[177] *Z. Elektrochem.*, 1920, **26**, 1, 25; *J.*, 1920, 229A.

[178] E.P. 141,925; *J.*, 1920, 448A.

[179] H. V. Thompson, *Trans. Cer. Soc.*, 1918-19, **18**, 510; *J.*, 1920, 230A.

[180] U.S.P. 1,323,735; *J.*, 1920, 517A.

By treating the sand with caustic soda the rare earths are obtained as hydroxides and the phosphoric acid recovered as the sodium salt.[182] O. Dietsche[183] separates thoria from the other rare earths by precipitation with a soluble fluoride in theoretical quantity.

TUNGSTEN.

Two methods of treating tungsten ores are described; C. J. Head[184] heats the ore with an alkali on an iron hearth and then filters off the fused alkali tungstate through a filter of iron turnings. J. B. Ekeley and W. B. Stoddard[185] fuse the ore with salt and soda together with silica or sodium nitrate and purify the aqueous extract of sodium tungstate by oxidising phosphorus and arsenic to phosphate and arsenate respectively by means of sodium hypochlorite and then precipitating them as the magnesium salts in presence of sodium chloride and ammonia.

O. J. Stannard[186] vaporises tin and tungsten as chlorides, by heating the ore with carbon in a current of chlorine. Hydrochloric acid extracts stannic chloride from the sublimate and precipitates tungstin trioxide.

ZINC CHLORIDE.

Metallic zinc reacts with organic chlorides such as carbon tetrachloride, tetrachloroethane, or hexachloroethane, sufficient heat being evolved to vaporise the zinc chloride produced. The reaction is initiated by a primer; a mixture of 3 parts of sodium nitrate and 2 parts of calcium silicide is excellent for the purpose; it may be mixed with gum arabic and spread on paper and lighted with a match. This method was used for the production of smoke clouds during the war. At a later stage when organic chlorides were scarce, zinc chloride itself was vaporised by the combustion of the priming composition.[187]

ZIRCONIUM.

An excellent account of the preparation of zirconia from zircite and of the preparation of the metal itself is given by J. W. Marden and M. N. Rich.[188] Coherent metal containing 99·4–99·5% of Zr was obtained by an alumino-thermic method.

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[181] U.S.P. 1,329,747; *J.*, 1920, 232A.

[182] Chem. Fabr. Heiligensee, G.P. 315,371; *J.*, 1920, 91A.

[183] U.S.P. 1,335,157; *J.*, 1920, 364A.

[184] E.P. 136,577; *J.*, 1920, 190A.

[185] U.S.P. 1,255,144; *J.*, 1918, 206A. E.P. 122,264; *J.*, 1919, 134A. E.P. 138,211; *J.*, 1920, 263A.

[186] E.P. 134,891; *J.*, 1920, 22A.

[187] E. Berger, *Comptes rend.*, 1920, **170**, 1492; **171**, 29; *J.*, 1920, 542A.

[188] *J. Ind. Eng. Chem.*, 1920, **12**, 651; *J.*, 1920, 596A.

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GLASS.

By W. E. S. Turner, D.Sc., M.Sc.,

Professor of Glass Technology, University of Sheffield.

DURING the year 1920 Germany, Czecho-Slovakia and Belgium began to affect once more the world's production of glassware.

In order to gain a clear idea of the present position of the glass ndustry and its technology, and especially of the probable effect of his competition from former enemy and from newly liberated countries, it is necessary to review not only the war progress, but also the position immediately before the war. Prior to the war the chief glassmaking countries of the world were Germany, Austria, Belgium, France, England, and the United States. In Asia, Africa, Australasia, and Central and South America the glass industry was a negligible quantity. These were importing countries. In our own country the distinctive branch was that of fine glass table ware, the best of which found a ready market even in the countries, such as Germany, which had gradually eaten into our glass trade as a whole. Sheet glass in England was produced by two large firms and by one or two much smaller firms; but the big sheet glass producing countries were Belgium, America, and Germany. Electric lighting glassware was made here to a comparatively small extent, Germany and Holland being the chief sources of supply. Of chemical glassware, none was made of any consequence except in Germany, including Bohemia. The centre for optical glass had for some time been Jena, the two other firms of note, one in Paris and one in England, having to take a back seat. Glass containers, bottles, and jars, as well as pressed glassware, were the products of other branches, carried on extensively in Germany, America, Belgium, Holland, Denmark, Sweden, France, and the United Kingdom. A little prior to the war these branches were beginning distinctly once more to make headway even in our own country. In England the application of science to the industry was, outside two large firms, but little known; there were practically no academic researches and no teaching, and almost no textbook. France appears to have been but little better off; America's technological developments were largely those of engineering. Only in Germany and Austria had there been, during the two generations prior to the war, notable achievements in the chemistry and physics of glass. Even there, advance was largely due to Jena.

The writer has not infrequently seen the laments of German technologists about the rule-of-thumb methods of the German glass industry. Still, Germany had a distinctive and important glass literature.

The position has changed rather radically since 1915. Under necessity other countries have had to try to meet their needs by manufacture and not by import. Whilst the production of fine table ware naturally declined, that of various articles of necessity has spread. Good chemical glassware was made during the war by four firms in this country, five in the U.S.A., at least two in France, whilst Sweden, Italy, and Japan have also contributed. Scientific glassware, made by blowing at the bench, began practically from nothing in this country, America, and Japan, and in the two former reached big dimensions. France contributed largely also, but the industry was not new. In optical glassmaking, the one French firm naturally exported greatly, and so did the existing British firm; whilst a second British firm, beginning in the middle of the war, has made very remarkable progress. In Germany a factory at Sendliger also made noteworthy progress. In America four firms began to make optical glass, and fair success was attained; but not more than two have continued since the war. Japan is known to have interested herself in optical glass, but what progress she has made is quite unknown. Little new development took place during the war in this country in the manufacture of sheet glass. Probably America gained most through the closing down of Belgian works. It is somewhat remarkable that Japan should have taken very rapidly to the production of window glass. The first plant of the wonderful Libbey-Owens system of window-glass drawing to be erected outside the United States was contracted for by Japan in 1919, although other processes had already been in successful operation in that country during the war. For electric light bulbs both America and Great Britain were, by the end of the war, self-supplying. This applies to illuminating glassware in general so far as America is concerned, but not to this country. The bottle and container industry has developed greatly, in spite of man-power shortage; American automatic or semi-automatic machinery has to a great extent taken its place. So it comes about that, whilst the United States, Canada, and Great Britain are in the position to do big export business in these branches, new factories, largely machine-operated, have been set in operation in Brazil, Argentine, Chile, South Africa, Australia (including Tasmania), China, Japan, and Spain. India is known specially to be seeking a development of the glass industry. Belgium and France are beginning to install glass-making machinery from America. Germany, Czecho-Slovakia, and

Austria up to the present moment have perhaps less automatic machinery than any of their immediate neighbours or trade competitors.

We have reached the position, therefore, that most of the great Powers have enormously developed their glassmaking resources. One or two additional countries have become practically independent so far as production capacity is concerned, some partly so. The question of markets, especially for export, therefore, becomes one of power to produce cheaply; and whilst this in turn is complicated by abnormal exchange rates and the cost of labour, it has become obvious that under steady conditions the scientific worker and the technologist must be called on to play an increasingly important part.

In this connexion it is hopeful to be able to record the remarkable burst of activity on the part both of Great Britain and America. Indeed, by comparison, published work of importance in other countries is almost negligible. Far more important glass researches have been published in these two countries during the past four years than had appeared in Germany in the last twenty. There is no doubt that in this country the work and the resources of the Department of Scientific and Industrial Research have been of very great value to the industry, in that they have made possible the work of the Department of Glass Technology at Sheffield, and more recently the Glass Research Association, as well as the provision for work at the National Physical Laboratory. The other stimulating influence in this country has been the Society of Glass Technology. In America the formation of a special Glass Division of the American Ceramic Society and of the new Optical Society of America with its excellent journal, now in its fourth volume, have served to focus and stimulate scientific work on glass. But it is true that the call to service during the war has found both countries provided with able scientific men capable of revolutionising the glass industry if given their opportunity.

Probably no year has seen the publication of so many papers of first-class importance as the year 1920. They are partly the fruit of war activities which it is only now possible to make known. Of more than ordinary interest are the papers involving the study of some aspect of optical glass, since they mark the breakdown of the traditional secrecy associated with this branch; and there is nothing more important at the present juncture, in the writer's view, than the frank discussion of general scientific problems in the industry in order to arouse and maintain interest amongst manufacturers, and so secure a new outlook.

Outside the statements in the report which follows (in the preparation of which the writer is much indebted to his colleague, Mr. F. W. Hodkin, B. Sc.), it only remains to say that the year has been marked, especially in this country, first by the rapid installation of machines for mass production, and secondly by the discussion of methods of meeting the competition from abroad due to the state of the exchanges. In regard to the former, a further number of Owens machines have been installed this year, a large number of O'Neill's, a smaller number of Miller, Lynch, and miscellaneous types for bottle, jar, and tumbler making. Five types of automatic feeding devices have been in active use during the year, and at least two others have had trials. The number of Empire machines and of Westlake machines for electric bulbs has been increased, and it is now expected that the Libbey-Owens glass tube-drawing machine will presently be in operation. In regard to sheet glass, the Libbey-Owens Company has made arrangements to set up the European parent works with twelve furnaces and twelve machines in Belgium, whilst works may be located in other European countries.

1920 has seen much discussion on the comparative merits of British and foreign scientific glass; certainly the retention and development in this country of the manufacture of optical and scientific glassware is earnestly desired by all scientific men who take a pride in British achievements and possibilities. 1921 will probably mark a decision as to whether or not these branches, developed with much enthusiasm during the war, can be retained as a British possession.

OPTICAL GLASS.

The great activity in this branch of the industry during the war period and that immediately following is now coming to light through the medium of scientific papers. Some of these are of fundamental importance. In this connexion special reference must be made to the series of nine papers by C. J. Peddle.[1] The results of the researches were used by him in the actual development of commercial types of optical glass. It is possible in this report to give only a very brief and inadequate outline of the field covered by the author. A vast amount of data has been accumulated concerning the effects of silica, sodium oxide, potassium oxide, calcium oxide, and lead oxide on the melting rates, colour, density, refractive index and dispersion, devitrification, solubility, and durability or weathering of the glasses, and also on pot attack. The glasses which are suitable for optical work are indicated and the modifications required for large scale meltings as compared with the small scale meltings described are discussed. The calculation of batches for optical glasses of given optical constants is explained. Of the silica-lime-alkali series the following glasses and others in their near vicinity can be used for general work :—100 SiO_2, 20 Na_2O, 20 CaO ; 100 SiO_2, 20 K_2O, 20 CaO ; 100 SiO_2, 10 Na_2O, 10 K_2O, 20 CaO. Each of the above glasses may be expressed by the simpler molecular formula 5 SiO_2,R'_2O,CaO and silica-lime-alkali glasses corresponding to this formula are believed by the author to be more suitable than those conforming to the Benrath formula, 6 SiO_2,R'_2O,$R''O$. The following silica-lead-alkali glasses of the molecular series 100 SiO_2, 20 R_2O, xPbO are of use :— 100 SiO_2, 20 Na_2O, 30 PbO ; 100 SiO_2, 20 Na_2O, 40 PbO ; 100SiO_2, 10 Na_2O, 10 K_2O, 30 PbO ; 100 SiO_2, 10 Na_2O, 10 K_2O, 40 PbO ; 100 SiO_2, 20 Na_2O, 15 PbO, 100 SiO_2, 20 Na_2O, 20 PbO ; 100 SiO_2, 10 Na_2O, 10 K_2O, 15 PbO ; 100 SiO_2, 10 Na_2O, 10 K_2O, 20 PbO. If a purely potash glass of this type is desired owing to higher brilliance, less than 11% of K_2O should be introduced. Useful glasses of other types were indicated, containing up to 50% of lead oxide. In the author's opinion it appears impossible to give a formula for an alkali-lead oxide-silica glass which will satisfy all requirements, but the formula 5 SiO_2,R'_2O,1·5 PbO will suit most of the conditions required by the manufacturer.

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[1] *J. Soc. Glass Tech.*, 1920, 4, 3-107, 299-366; *J.*, 1920, 545A.

R. J. Montgomery,[2] from a study of published information combined with practical experience, found that by plotting the dispersions and refractive indices of optical glasses as abscissæ and ordinates, respectively, the glasses fell into natural groups on the plotted field. Twenty-three ordinary types of optical glass are thus obtained, each type representing a number of glasses closely allied as regards optical properties, composition, and method of manufacture. The glass components may be divided into two sections, first, the fundamental oxides SiO_2, K_2O, Na_2O, PbO, CaO, ZnO, B_2O_3, etc., which affect the optical properties, and secondly, the control chemicals, that is the proportioning of carbonates, nitrates, sulphates, chlorides, and the use of arsenic and antimony, which affect the melting operations. The glasses include those with refractive indices from 1·45 to 1·80 and dispersions from 20·0 to 70·0.

Certain relations between chemical composition and refractivity in optical glasses have been investigated by F. E. Wright.[3] The several factors involved are presented chiefly in graphical form. The dispersion relations alone are first considered, after which the chemical characteristics and the relations between chemical composition and optical constants are treated in summarised diagrams to indicate the methods adopted, which enabled the author to solve the problems in a practical way in a short time. No consideration was given to the more fundamental problem of computing the optical constants of a glass of given chemical composition. In this connexion, however, the papers of C. J. Peddle[4] and also one by J. R. Clarke and W. E. S. Turner,[5] relating to the soda-lime glasses, are of importance. These authors find that the refractive index for the D line is practically an additive property of the composition. The refractive indices undergo regular increases as CaO replaces Na_2O, but the total and partial dispersions and values of ν are practically constant throughout this series of glasses.

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[2] *J. Amer. Cer. Soc.*, 1920, **3**, 404 ; *J.*, 1920, 572A.

[3] *J. Amer. Cer. Soc.*, 1920, **3**, 783 ; *J.*, 1921, 10A.

The physical properties and annealing of optical glasses have received considerable attention. A. Q. Tool and J. Valasek,[6] during a comprehensive study of the annealing of glass, obtained definite and clear information of an increase in the rate of heat absorption by glass at the softening point. This phenomenon, already previously indicated but not generally known, was shown by the authors to be detectable not only by a differential thermocouple but also by the inverse rate of cooling method such as is employed in the study of iron and steel. Corresponding evolution of heat occurs during the cooling process.

C. G. Peters and C. H. Cragoe[7] have determined the dimensional changes of glass in the annealing and higher temperature region in order to find, if possible, the cause of the strain introduced while cooling through the annealing range and to demonstrate any relation which might exist between the dilatation and the heat absorption found by Tool and Valasek.[8] The thermal dilatations of thirty-two different kinds of glass have been measured by means of the Fizeau-Pulfrich interferometer at temperatures from 20° to 675° C. The results indicate the temperature for the best and most thorough annealing, the region where very careful cooling is essential, and also the upper temperature limit for rapid annealing. A critical expansion region exists for each glass. This region does not exceed 40° C. for any of the glasses examined but the rate of expansion increases two to seven fold. With a barium crown glass this critical region occurs at about 400° C., but with a lead glass at 575° C. The glass softens and contracts when the temperature has increased to about 75° C. above the critical region. A comparison of results shows that the heat absorption observed by Tool and Valasek occurs in the same temperature region as the critical change in expansion. The cooling of optical glass in the pot involves a greater amount of labour and waste than rolling into a sheet, but glass of the highest quality is obtained. H. S. Roberts[9] discusses this problem and indicates that convection may be reduced by insulating the upper portion of the melt with a layer of kieselguhr

[4] *Loc. cit.*

[5] *J. Soc. Glass Tech.*, 1920, **4**, 111 ; *J.*, 1920, 545A.

[6] *U.S. Bureau of Standards, Sci. Paper* 358.

[7] *U.S. Bur. Standards, Sci. Paper* 393 ; see *J.*, 1920, 572A.

[8] *Loc. cit.*

[9] *J. Amer. Cer. Soc.*, 1919, **2**, 543 ; *J.*, 1919, 721A.

or other light insulator and cooling rapidly from the bottom. It may be further reduced by intensive chilling of the bottom of the pot by means of a current of compressed air or a fine stream of water during the last hour before it is removed from the melting furnace. Through the annealing range the cooling rate can be reduced by placing the pot in an enclosed space and heating the air round it, or by surrounding the pot by insulating material. The rate of cooling through the annealing range determines the size and shape of the pieces into which the melt will break.

The rolling of optical glass into sheet has advantages, however, as indicated by H. S. Roberts and J. C. Hostetter.[10] The pot of metal, melted in the usual way, is stirred in a large circle at low speed and subsequently treated as plate glass. There is great saving of pots, pot-arching, waste in cutting and time, and polishing and cutting to size are easily accomplished. The uses of this glass are obviously somewhat restricted, but it is suitable for the large-scale production of photographic lenses, field-glasses, spectacles, etc.

A further method for determining the annealing temperature of glass is described by J. T. Littleton and E. H. Roberts.[11] The authors assume that the rate of annealing is proportional to the viscosity, and having ascertained the annealing temperature of a standard glass and its viscosity at that temperature they assume that the annealing temperature of any glass was the temperature at which it had this viscosity. The method of determining the viscosity is described and it is also found that the maximum and minimum annealing temperature can be obtained from the viscosity measurements. The authors found their assumptions justified in practice.

The detection and effects of striæ in optical glass are dealt with by T. T. Smith, G. G. Merritt, and A. H. Bennett[12] and also by L. E. Dodd.[13] In the first paper the methods of detecting striæ are described and illustrated by photographs obtained by a highly sensitive process. It is found that the refractive indices of striæ differ from those of the surrounding glass by 2 in the fourth decimal place. The authors conclude that in most visual work a few striæ are objectionable only when in focus, or nearly so, in the field of view. The second paper deals with comparison tests for striæ by the Brashear converging light, direct view, Bureau of Standards tank immersion, and short range projection methods. The author finds for samples with polished ends, that the short range projection method is the best for regular use. A line of light 2·4 mm. long and 0·5 mm. wide is projected from a specially-shaped lamp through the glass under examination on to an opal-backed sheet of plate glass. Shadows of any striæ are projected on the opal glass screen.

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[10] *J. Amer. Cer. Soc.*, 1920, **3**, 750.

[11] *J. Opt. Soc. Amer.*, 1920, **4**, 224.

[12] *U.S. Bur. Standards, Sci. Paper* 373.

[13] *J. Amer. Cer. Soc.*, 1919, **2**, 977 ; *J.*, 1920, 335A.

G. W. Morey[14] publishes an abstract from the report of a committee on the classification and nomenclature of optical glass. The system proposed is based on the crown-flint series of barium-free glasses. A v value of 56 is adopted to divide the flints from the crowns. Three sections are used in the crown series, ordinary crowns (v between 56 and 61), borosilicate crowns (v greater than 61), and fluor-crowns (v greater than 68). The five classes of flints are the extra dense flints, dense (v between 31 and 34), medium (v from 34 to 38), light (v from 38 to 50), and extra light (v from 50 to 56). Grouped with the barium crowns and flints are glasses which fall outside the above series and these comprise barium crowns with n_D above 1·60, light barium crowns with n_D from 1·54 to 1·60, light barium flints with n_D below 1·60, medium with n_D between 1·60 and 1·64, and dense barium flints.

Two papers by F. R. von Bichowsky on the durability of glass are worthy of note. In the first,[15] the author recommends a slightly modified form of Mylius' iodeosin test by which a quantitative value was obtained, termed the surface alkalinity constant. On the basis of this constant glasses were grouped in five classes. Heating in bomb tubes with various solutions and subsequent examination of the surfaces of the glasses when wet and dry was used to determine the rate of solubility of glass in various agents. In the second paper[16] a theory of the mechanism of the action of water on glass is advanced. The true adsorption of water on the surface is followed by the diffusion of the adsorbed water into the body of the glass. This water then reacts with the glass and forms a surface film, which in turn soaks up water and induces further action. The soluble salts from the surface film, alkaline carbonates and hydroxides form a strongly alkaline solution which dissolves the silica skeleton film.

THE PHYSICAL PROPERTIES OF GLASS (OTHER THAN OPTICAL GLASS).

S. English and W. E. S. Turner have investigated the thermal expansions of soda-lime-silica glasses[17] and soda-magnesia glasses.[18] They find that in a series of lime-soda glasses of generally similar type, the variation of the composition and the coefficient of expansion are related to one another in a simple additive manner; those glasses with highest soda content have the greatest rate of expansion, and successive increase in the lime content with diminution of soda reduces the expansion. Considerable errors are found in Schott's factors for the calculation of coefficients of expansion. Similarly in the magnesia-soda series of glasses the coefficients of expansion are found to be an additive property of the composition. Replacement of soda by magnesia causes rapid diminution in the thermal expansion, magnesia being much more effective than lime in this respect. New factors have been deduced for soda-lime and soda-magnesia glasses, leading to closer agreement between observed and calculated expansions than can be obtained by Schott's factors. The expansion of various kinds of glass from ordinary temperatures up to 750° C. has been measured by W. B. Pietenpol.[19] It is found that the rate of expansion of annealed glass is nearly linear up to 450°–550° C.; it then increases by from four to six times for the next 60°–100° C. From this point it again becomes linear until the softening point is reached when it gradually decreases until the glass loses its form. Results with unannealed glass show that the rate of expansion first decreases due to the relieving of internal strain, then the glass behaves as annealed glass except that on cooling a shrinkage occurs, the amount depending on the strain which has been relieved.

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[14] *J. Opt. Soc. Amer.*, 1920, **4**, 205.

[15] *J. Amer. Cer. Soc.*, 1920, **3**, 296; *J.*, 1920, 546A.

[16] *Ibid.*, 309; *J.*, 1920, 545A.

[17] *J. Soc. Glass Tech.*, 1919, **3**, 238; *J.*, 1920, 407A.

[18] *Ibid.*, 1920, **4**, 115; *J.*, 1920, 546A.

It is shown by S. English and W. E. S. Turner[20] that Winkelmann and Schott's density factors lead to calculated results much too low for soda-lime glasses and further that the densities obtained for two low-lime glasses are very distinctly higher than those quoted by E. W. Tillotson.[21] Their results prove that substitution of soda by lime in a glass causes a rise in density, the density being, approximately, an additive function of the composition. With soda-magnesia glass, the same authors[22] find that as the proportion of magnesia increases and that of soda decreases, the density diminishes, but is again an additive function of the composition. C. J. Peddle[23] confirms the results obtained but points out that when magnesia is added to a glass and not used as a substitute for soda, the density of the glass may increase.

The method for determining the annealing temperature of glass as suggested by J. T. Littleton and E. H. Roberts[24] has already been mentioned. M. So[25] shows that the relation between the temperature and time required for the annealing of borosilicate glass, soda glass, lead glass, and soda-lead glass is a logarithmic one, expressed by the equation $H = aT^n$ when H is the annealing time, T the annealing temperature, and a and n constants depending on the composition of the glass and the degree of its internal strain. The annealing temperatures of magnesia-soda glasses are dealt with by S. English and W. E. S. Turner,[26] who find that the rate of increase of annealing temperature is, for the softer glasses, less with the magnesia series than with the lime series.[27] With the hardest glasses, however, there is a suggestion that the curves for still higher proportions of lime and magnesia may approach or even intersect one another. The same authors, together with F. W. Hodkin and C. M. M. Muirhead,[30] show that the gradual addition of silica in the sodium silicate glasses leads at first to a rapid rise of annealing temperature. This rise is not maintained, however, and high annealing temperature may not, therefore, be associated with high silica content. G. V. Wilson[28] and S. English[29] describe somewhat similar instruments for the detection of strain in glass, both of simple construction.

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[19] *Chem. and Met. Eng.*, 1920, **23**, 876; *J.*, 1920, 748A.

[20] *J. Soc. Glass Tech.*, 1920, **4**, 126; *J.*, 1920, 546A.

[21] *J. Ind. Eng. Chem.*, 1912, **4**, 246.

[22] *J. Soc. Glass Tech.*, 1920, 4, 153; *J.*, 1920, 627A.

[23] *Ibid*, 1920, **4**, 281; *J.*, 1920, 783A.

[24] *Loc. cit.*

[25] *Proc. Phys.-Math. Soc. Japan*, 1920, [3] 2, 112.

The viscosity of glass, whilst extremely important in so many ways in glass manufacture, has scarcely received the attention it merits. E. W. Washburn[31] suggests a factory method for measuring the viscosity of pot-made glass during the process of manufacture. A stirring cylinder is operated directly by a motor, the power consumption of which, P, where the angular velocity of the stirring cylinder is ω, can be determined. If k is the calibration constant of the pot and P_0 the power used in overcoming any mechanical and electrical friction in the driving mechanism, the viscosity, y, is given by the equation $y = k(P-P_0)w^2$.

An interesting series of measurements has been made by R. Ambronn[32] of the electrical conductivity of thirteen different glasses containing only Na_2O, CaO, and SiO_2. He shows that the relation between conductivity and temperature can be expressed by a simple exponential equation in which the exponent is the reciprocal of the absolute temperature, and that the conductivity is zero unless the sum of the calcium and sodium atoms is at least 11 to each 100 atoms of the glass substance; in this connexion 1 atom of Na is equivalent to 1 atom of Ca.

Glass Making.

The potash situation, though not so acute, still demands attention. E. C. Rossiter and C. S. Dingley[33] estimate that potassium salts equivalent to 60,000 or even 80,000 tons of potassium chloride per annum are recoverable from the blast furnaces of England and Wales. In connexion with the shortage of supply of salt cake it is interesting to note that four Siberian lakes[34] are estimated to contain upwards of seven million tons of sodium sulphate.

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[26] *J. Soc. Glass Tech.*, 1919, **3**, 278; *J.*, 1920, 407A.

[27] *Ibid.*, 1919, **3**, 125; *J.*, 1919, 722A.

[28] *Ibid.*, 1919, **3**, 246.

[29] *Ibid.*, 1919, **3**, 258; *J.*, 1920, 407A.

[30] *Ibid.*, 1920, **4**, 000.

[31] *J. Amer. Cer. Soc.*, 1920, **3**, 735.

[32] *Ann. Physik*, 1919, [4], **58**, 39, 175; *J.*, 1920, 295A.

[33] *J.*, 1919, 375T.

Papers furnishing information concerning the preparation and working properties of soda-lime and soda-magnesia glasses are published by J. H. Davidson and W. E. S. Turner[35] and J. H. Davidson, F. W. Hodkin, and W. E. S. Turner[36] respectively. The glasses were based on the trisilicate molecular formula,

$$3\,SiO_2, x\,CaO \text{ (or } MgO), y\,Na_2O \text{ where } x + y = 1.$$

With this series as the percentage of lime increases devitrification occurs less readily when the glass is used for lamp-working purposes. Glasses which are of use for semi-automatic machines, pot metal, and for tanks operated by hand labour are indicated. Magnesia resembles lime in some respects as regards its influence on glass. It bestows greater viscosity than lime, diminishes rate of cooling, and reduces the coefficient of expansion and the annealing temperature. There is a tendency to raggedness or stringiness when working magnesia glasses which is not shown by lime glasses. The durability of soda-lime glasses of series already mentioned has been examined by J. D. Cauwood, J. R. Clarke, C. M. M. Muirhead, and W. E. S. Turner.[37] Tests were made in water, hydrochloric acid, caustic soda, and sodium carbonate. Glasses produced from batches varying between (*a*) sand 1000, soda ash 590, and (*b*) sand 1000, soda ash 441, limespar 139, are unsatisfactory, being too readily attacked by all the reagents, and are hygroscopic. Gradual substitution of soda by lime increases the stability of the glass to all kinds of liquids. The choice of glass batches containing lime, for making bottle glass, is considered by W. E. S. Turner.[38] Batches with a high lime content, since the glass produced sets quickly, are highly suitable for hand working and for certain semi-automatic machines. For the modern, highly productive machines a batch, the composition of which might lie between sand 1000, soda ash 412, limespar 166, and sand 1000, soda ash 353, and limespar 222 is generally suitable. The percentage of lime in the glass should not fall below 7·5.

R. L. Frink[39] gives a summary of the essential conditions for the successful melting of glass in tank furnaces. Dealing with the same subject, M. W. Travers[40] gave data concerning some special glasses and referred particularly to the alumina percentage of the glass.

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[34] *U.S. Com. Rep.*, Nov., 17, 1919.

[35] *J. Soc. Glass Tech.*, 1919, **3**, 222 ; *J.*, 1920, 407A.

[36] *Ibid.*, 1919, **3**, 275 ; *J.*, 1920, 407A.

[37] *Ibid.*, 1919, **3**, 228 ; *J.*, 1920, 407A.

[38] *J. Amer. Cer. Soc.*, 1920, **3**, 379 ; *J.*, 1920, 572A.

[39] *J. Soc. Glass Tech.*, 1919, **3**, 242 ; *J.*, 1919, 394R.

[40] *Ibid.*, 1919, **3**, 253 ; *J.*, 1920, 407A.

Three series of lead-soda, lead-potash, and lead-soda-potash glasses of commercial value for table ware have been prepared and tested by F. W. Hodkin and W. E. S. Turner.[41] The lead-soda glasses melt most readily, the lead-potash least readily ; the lead-soda-potash glasses, with soda and potash in equivalent proportions, fine most readily ; the lead-potash glasses are the most viscous and the lead-soda least. The colour of the glasses is most marked with soda and least with the potash series. The addition of two parts of borax per 100 parts of sand exercises a beneficial effect on the durability and a mixture of alkalis is preferable to either alkali alone for all-round purposes. This latter point is confirmed by C. J. Peddle[42] in his paper on the development of glasses. The manufacture of sheet and plate glass, particularly the reinforced type, has made considerable progress. E. H. Bostock[43] outlines the history of the sheet glass industry in America. The most successful development appears to be that of the Colburn process by the Owens Company. The author indicates in detail the lines along which further development is essential. Two patents taken out by L. F. Mascart[44] relate to the production of unshatterable glass by means of a core of celluloid. A patent for similar glass is due to C. S. and V. Shuman.[45] P. B. Crossley[46] suggests the manufacture of a non-fragile glass using natural silicates such as micaceous mineral, asbestos, and the like. A mixture of the finely-divided silicious material and powdered glass or a similar vitreous substance is melted just sufficiently to enable the mass to be rolled or forged. The product, it is claimed, may be transparent, semi-transparent, or opaque ; it can be turned, adheres tenaciously to metals, and is very suitable for electrical and heat insulators etc.

An account of some experiments with glasses for lamp-working is published by J. D. Cauwood, J. H. Davidson, F. W. Hodkin, and W. E. S. Turner.[47] The composition and properties of certain German, Austrian, and French glasses are discussed. The discoloration produced by lead, antimony, and arsenic in lamp-working tubing has been investigated by F. W. Hodkin and W. E. S. Turner,[48] who find that arsenious oxide and antimony oxide are very potent in causing discoloration when the glass is worked in the flame. These compounds are more effective than lead oxide ; between 2 and 5 parts in 10,000 of these oxides are sufficient to cause discoloration whilst 0·6% of lead oxide is necessary.

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[41] *J. Soc. Glass Tech.*, 1920, **4**, 120 ; *J.*, 1920, 421A.

[42] *Loc. cit.*

[43] *J. Amer. Cer. Soc.*, 1920, **3**, 35.

[44] U.S.P. 1,342,267-8 ; *J.*, 1920, 519A.

[45] U.S.P. 1,324,361.

[46] E.P. 152,780 ; *J.*, 1920, 820A.

[47] *J. Soc. Glass Tech.*, 1919, **3**, 266 ; *J.*, 1920, 407A.

[48] *Ibid.*, 1920, **4**, 158 ; *J.*, 1920, 627A.

COLOUR AND COLOURED GLASSES.

Sir H. Jackson[49] in a comprehensive paper deals with the plasticity and coefficient of expansion of glass as related to the sealing of wires in glass; the structure of glass and the phenomena of crystallisation; occlusion of gases, phosphorescence and allied problems. The production of various types of opal glass is briefly discussed, also the production and properties of glasses containing gold, copper, and selenium. Gold gives colours varying from red through the purples to blue; copper, in the metallic state, gives a red normally but will give variations similar to gold, even to a definite blue, by transmitted light. Interesting experiments are described which throw some light on the development of the pink or violet colour in window glass. Nickel and cobalt glasses and the various colours obtainable are also discussed. The production of selenium red glass is described by F. A. Kirkpatrick and G. R. Roberts.[50] The batches, methods of working, temperatures of glory-holes and lehrs are given and diagrams showing the effect of specimens on the prismatic solar spectrum. The colours of colloids, glasses, glazes, and gems form an instructive study by W. D. Bancroft.[51] A glass containing gold, when quickly cooled, is colourless, probably due to the presence of gold in a true solution or to its particles being too small to have an optical effect. H. Jackson[52] also suggests the former possible explanation. The action of carbon in producing a yellow colour in glass is treated historically and experimentally by Springer,[53] who concludes that the colour is due to carbon in a colloidal condition.

M. Luckiesh[54] has investigated the transmission factor for total visible radiation for various coloured glasses at temperatures below that at which they become self-luminous or plastic, and finds that generally the transmission diminishes with rise of temperature. Cobalt-coloured glass is an exception. The results for ten commercial specimens are given, the colouring elements being copper, cobalt, gold, manganese, and chromium. More than fifty glasses have been examined by K. S. Gibson, G. P. T. Tindall, and H. J. McNicholas,[55] and the transmission values determined photographically, visually, and, in most cases, photo-electrically. The uses of the glasses are indicated such as for ultraviolet and railway signalling, improvement of visibility for visual and photographic work, eye protection, selective absorption, and for obtaining monochromatic light from mercury, hydrogen, or helium lamps. S. C. Lind[56] discusses the colouring and thermoluminescence of glass produced by radium emanation. A patent of M. Luckiesh and D. A. Dewey[57] deals with the production of integral glass screens which act as colour filters adapted for use in conjunction with artificial light for the production of an approximation to daylight. The batch is given and the patent covers any blue glass to produce daylight effects containing copper, manganese, and cobalt. M. W. Gleason[58] has invented a method for the production of laminated glass, the various laminations being so chosen that when the compound glass is used as an electric lamp globe it produces a light very similar to natural daylight. The molten glass from which the several laminæ are formed is assembled by the blower dipping his pipe first into blue, then into opal, and finally into clear glass.

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[49] *J. Soc. Roy. Arts*, 1920, **68**, 134.

[50] *J. Amer. Cer. Soc.*, 1919, **2**, 895; *J.*, 1920, 110A.

[51] *J. Phys. Chem.*, 1919, **23**, 603, 623.

[52] *Loc. cit.*

[53] *Sprechsaal*, 1919, **52**, 88; *J.*, 1919, 820A.

[54] *J. Amer. Cer. Soc.*, 1919, **2**, 743; *J.*, 1919, 903A

[55] *U.S. Bur. Standards, Tech. Paper* 148.

FURNACES AND LEHRS.

The use of the Owens machine has frequently been decided against owing to the high consumption of fuel on the revolving glass trough. J. S. Atkinson, Messrs. Stein and Atkinson, and T. C. Moorshead[59] have patented a glass furnace of the kind in which a rotating table and trough, for the most part within the furnace, carry the glass to a gathering or removal point just without the furnace. In this furnace a gas and air recuperator or a separate gas or air recuperator is employed in which the waste products flow horizontally to the outlet chamber, and the air or gas to be heated flows vertically without change of direction. This furnace should stimulate still further the use of the Owens machine.

Three furnaces of somewhat novel design as regards firing are worthy of note. A patent by Fours et Procédés Mathy[60] describes a pot furnace with a number of separate chambers arranged in a row, each chamber containing a pot. Each pot is surrounded with fragments of porous refractory material, similar material being placed in cavities in the base of the chamber, to which gas and air are supplied for flameless combustion. Beneath each chamber is a regenerator for the air. Molten glass, escaping from a broken pot, flows down into the air passage, and thence into a chamber at the side of the regenerator through a passage which is normally closed by a thin plate of fusible alloy. A regenerative furnace, patented by S. G. Curd,[61] is fired with producer gas, which is passed over a mixture of iron and carbon before entering the furnace to enrich and improve the heating qualities of the gas. It is further enriched by mixing it with gaseous products such as hydrogen and carbon monoxide, obtained by passing superheated steam over a similar mixture of iron and carbon. H. Wilkinson[62] has produced a glass-pot furnace having a grate beneath its eye. Means are provided for supplying solid fuel to the grate, and a recuperator is used for preheating the secondary air before it enters the eye. The patentee claims that this furnace can use an inferior coal, and that it requires less fuel and attention than either the old English or the Hermansen furnaces.

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[56] *J. Phys. Chem.*, 1920, **24**, 437 ; *J.*, 1920, 628A.

[57] U.S.P. 1,331,937 ; *J.*, 1920, 296A.

[58] U.S.P. 1,342,282.

[59] E.P. 141,617 ; *J.*, 1920, 408A.

[60] E.P. 135,115 ; *J.*, 1920, 25A.

[61] E.P. 135,636 ; *J.*, 1920, 65A.

A Dutch firm[63] has designed a furnace of the tank type fired with liquid fuel. The jet of liquid fuel is driven into the furnace at the working end, and under pressure so regulated that the highest temperature is developed at a distance from the burner at the melting end of the furnace where the fresh batch is filled in. In this way the jet of fuel on entering the furnace passes over the molten glass and not over the cold, freshly filled batch which might otherwise take up carbonaceous matter and consequently yield discoloured glass.

The Dennis Simplex furnace is described in detail by M. W. Travers.[64] The original furnace was gas-fired with two producers in the centre, flanked by recuperators. On rebuilding the furnace the producers were replaced by the Frisbie under-feed grate, and it is claimed that a remarkable increase in efficiency has resulted.

The production of sheet glass direct from the tank continues to attract attention. One tank[65] designed for the purpose contains within it a glass drawing well formed of refractory shields and a pair of movable refractory blocks provided with fluid conduits, and with their opposite faces spaced apart to an increasing distance at the glass line as the blocks are increasingly immersed. Suitable means are also provided for drawing a sheet of glass from between the blocks in a plane at right-angles to their faces. H. Douchamp[66] claims a furnace provided with a number of drawing stations, each consisting of a doghouse projecting into the body of the tank, and formed by vertical blocks of refractory material suspended from girders.

The form of setting of regenerators, their advantages and method of cleaning, have been dealt with by a number of investigators, as, for example, by F. J. Denk,[67] who discusses the two essential requirements for regenerating chambers. It is shown that the temperature of combustion decreases with increasing excess of air, and that the highest flame temperatures are obtainable with the theoretical quantity of air. Producer gas cannot be burned in present furnaces without excess of air, but the excess should not exceed 25%.

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[62] E.P. 143,125; *J.*, 1920, 490A.

[63] N. V. Glasfabriek Leerdam, G.P. 314,605; *J.*, 1920, 267A.

[64] *J. Soc. Glass Tech.*, 1920, **4**, 205.

[65] B. G. Bealor, U.S.P. 1,331,796; *J.*, 1920, 296A.

[66] U.S.P. 1,298,474; *J.*, 1919, 465A.

[67] *National Glass Budget*, 1919-20, [28], 1; 1919-20, [29], 1.

H. Hecker and Co.[68] have a regenerator of the kind in which air ducts are arranged parallel to and on all sides of waste gas ducts, the air ducts being built up of tubular bricks of approximately hexagonal shape in cross-section. They are arranged in horizontal and vertical rows so as to form waste gas flues which are square in cross-section. A general discussion[69] has taken place between G. Suchy, J. Baldermann, M. Rubolt, and others on the relative merits and demerits of the method of setting regenerators on movable carriages, and the question of cleaning regenerators.

Muffle lehrs are the subject of many patents. F. J. Denk[70] in his description of the Simplex muffle lehr, indicates the following disadvantages found in the average open type of lehr : (1) glass cannot be satisfactorily annealed owing to the arch being further away from the glassware in the centre of the lehr than at the sides ; (2) to obtain sufficient heat to anneal the glass properly in the centre of the lehr, it is often found that the glass at the sides is melted down ; glassware from an open-type lehr, whether the lehr is fired by producer gas or fuel oil, is always covered by a bloom. The Simplex lehr has a flat arch supported by cast iron permitting the use of thin tiles and accordingly increasing radiation and decreasing fuel consumption. A simply constructed burner is in the top of the fire-box, the flame being drawn down either side and underneath the pans ; it is also in an easily accessible position and ensures a self-cleaning fire. It is claimed that draught control and a system of dampers ensure uniform and economical distribution of the heat and easy transference.

An annealing furnace for lampworked articles, invented by G. R. Hughes,[71] is arranged close to the lampworkers' bench and is provided with a separate door for each worker. When the door is opened by a pedal etc., blowpipes are automatically turned on inside so as to heat the air which enters when the door is opened. A separate conveyer track may be provided for each door.

GLASSWORKING MACHINERY.

The expiration of the Brooke patents[72] for glass flowing devices has stimulated and encouraged the production of many types of feeding devices. K. E. Peiler (Hartford Fairmont Co.[73]), has invented a machine for feeding glass from a tank or pot in portions of uniform size, consistency, and temperature, and delivering them without any undue chilling. The glass is gathered on a head made of highly refractory material and the process of gathering follows that of hand gathering very closely. In many gravity feeders the ingenuity of the inventors has mainly been devoted to methods for arresting the flow when sufficient molten glass has been delivered. One form[74] consists of two reciprocating blocks of manganese steel or compressed carbon used for chilling the glass at the moment of shearing off. Removal of the chilling blocks immediately after shearing allows time for the chilled skin of glass to be reheated by the internal heat of the metal, and downward movement commences again for the next delivery. Another type[75] severs and restarts the flow by means of a movable lip or flow block extending from a doghouse built on to the nose of a tank. The glass may flow vertically downwards into a mould or it may be diverted and carried back to the furnace. B. D. Chamberlain (Empire Machine Co.[76]) has invented a device allowing molten glass to flow from a tank through a discharge orifice, terminating in a cavity in the floor of the tank. The object of an invention due to W. A. Lorentz[77] is to provide means for transferring gatherings of glass from a gathering apparatus to the moulds of various machines in a substantially horizontal plane, thus avoiding the necessity of bringing the moulds directly beneath the glass outlet. Another patent[78] provides an outlet for molten glass, in a furnace, fitted with several nozzles made of steel and lined with refractory material. These are rotated so that each nozzle is used in turn and after each nozzle has been used it is heated and all adherent glass is removed so as to avoid the production of defects or marks in the glass. The British Thomson-Houston Co. and J. Gray[79] have patented a machine for manufacturing glassware, more especially bottles, lamp bulbs, etc., predetermined quantities of glass being discharged periodically from a tank or fore-hearth by a reciprocating displacer which is lowered into the tank to raise the level of the metal. Various devices have also been invented for overcoming the trouble due to chilling caused by dipping the tool into the glass in gathering, by the use of suction moulds. The foregoing patents are quoted not necessarily as the best but as representative devices showing the great variety of methods which may be adopted for feeding glass to machines.

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[68] E.P. 133,045.

[69] *Sprechsaal*, 1919, 52.

[70] *National Glass Budget*, 1919-20, [2], 1.

[71] E.P. 132,852 ; *J.*, 1920, 863A.

[72] E.P. 24,324 and 24,333, 1901.

[73] U.S.P. 1,324,464.

[74] U.S.P. 1,311,474.
[75] U.S.P. 1,312,876.
[76] U.S.P. 1,323,450.
[77] U.S.P. 1,300,180.
[78] E.P. 142,365.
[79] E.P. 131,756.

The drawing of glass cylinders for window glass has been responsible for a great number of patents and a smaller number have relation to the drawing of sheet direct from the tank. Bottle-machines have been modified in many cases and a number of new ones produced. The Owens Bottle Co.[80] patent a device relating to the manufacture of bottles having re-entrant bottoms. An automatic, self-feeding, bottle-making machine by T. Stenhouse[81] should also be mentioned. Pressing machines have also received considerable attention, W. E. Evans and M. J. Owens[82] being responsible for a type of automatic machine in which a number of complete units or working heads are carried by a rotating framework and in which the metal is gathered from the tank, shaped, and the finished article discharged automatically by each unit as it rotates. A patent by J. H. Groth[83] relates to means for pressing glass articles having recesses or apertures such as holders for cut flowers.

A Libbey Glass Co.[84] patent deals with apparatus for continuously drawing a rod or tube of glass from a forming apparatus and successively severing it into sections or predetermined lengths.

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[80] E.P. 132,768.

[81] U.S.P. 1,297,412.

[82] E.P. 142,007.

[83] U.S.P. 1,290,738.

[84] E.P. 140,440.

REFRACTORY MATERIALS.

By W. E. S. Turner, D.Sc., M.Sc.,

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The year that has passed has been characterised by steady progress rather than outstanding events in the development of the scientific study and manufacture of refractory materials. It has been a distinctly encouraging feature that manufacturers have not been content to rest on their war achievements; rather, indeed, the inquiring mind and the disposition to learn have been on the increase. On their part, scientific workers have not lacked in response. It is a pleasure to be able to record the establishment of another research centre in this country, namely, at Brierley Hill, Staffordshire, a convenient centre for the Stourbridge and district fireclay refractories manufacturers. Further, the Refractories Research Association, alluded to in last year's report, is now getting actively into work.

Two sets of valuable Government publications of interest to the student of refractory materials may be referred to. The first is the set of reports on minerals, including magnesite and chromium ores, which have been issued under the auspices of the Imperial Mineral Resources Bureau, the committees of which were active last year. The second, and relatively more important in connexion with this report, is the new volume published by the Geological Survey, namely Vol. XVI. of the special reports on the mineral resources of Great Britain, dealing with ganister and silica rock, sands for open-hearth steel furnaces, and dolomite. This report should be read by all who are interested in those particular industries.

General (Mainly Fireclay Refractories).

The selection of refractories for industrial uses is receiving greater attention now than ever before and, as W. F. Rochow[1] points out, a superficial consideration of the chemical and physical properties of a refractory material is not sufficient, and is often misleading. Good results are frequently obtained from products of which the chemical composition and physical properties at first sight appear to make them unsuitable. Rochow states that the spalling of silica bricks may be reduced, and often eliminated, by heating and cooling slowly through the critical range at which most of the expansion occurs. With fireclay and magnesia refractories there is a considerable difference between the softening and melting points. In the case of silica, however, this difference is only small, so that deformation does not occur until the melting point is almost reached. Therefore, in arches, silica bricks with a covering of kieselguhr or other insulating material are quite efficient, whilst fireclay bricks would gradually soften and collapse. The actual temperature at which bricks are deformed when heated under a load of 25 lb. per sq. in. is a suitable indication of their usefulness. The specific gravity is a criterion of the extent to which the permanent expansion should be carried at the first firing.

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[1] *J. Ind. Eng. Chem.*, 1919, **11**, 1146; *J.*, 1920, 111A.

The lack of definiteness in the classification of clays and the consequent confusion which arises are discussed by A. S. Watts.[2] He suggests a classification based on five properties, namely, colour, shrinkage, bonding strength, vitrification, and fusion, the last two properties being possibly combined under the term "refractoriness." Various standards are also suggested for the properties mentioned.

R. M. Howe,[3] reporting the work of the technical division of the Refractories Manufacturers' Association (U.S.A.), states that the greater the proportion of water used in preparing the clay paste, the greater will be the strength of the burned product, and the less the porosity. An excess of water beyond that required for good working reduces the strength, but its effect on the density is not so great as the use of too little water. The strength of the product is also increased by long pugging. Slow drying is superior to rapid drying. Porosity/burning temperature curves give information as to the necessary heat treatment and indicate how the product is likely to behave in service.

The effect of treatment is also dealt with by H. W. Douda.[4] He finds that the dry strength of clays can be increased 76·2 to 675·0% by wet grinding for two hours. The addition of 1% of caustic soda and then wet grinding gives an increase, additional to that previously mentioned, of 19·1 to 78·3%; 1% of dextrin gives an increase of 16·1 to 52·6%, whilst the removal of coarse material by screening through a 150-mesh sieve gives an increase of 24·0 to 35·5%. A combination of the four treatments causes an increase in the dry strength of 188 to 2050%. Plasticity is increased by wet grinding, screening, and the addition of dextrin, but caustic soda causes the clay to become tougher in the plastic condition, and hence more difficult to mould. Scum was noticed on the clay in certain cases where soda was used and where wet grinding was not used, but this can be overcome by the use of a smaller quantity of soda or by the use of dextrin. Wet grinding increases the drying

[2] *J. Amer. Cer. Soc.*, 1920, **3**, 247; *J.*, 1920, 490A.

[3] *J. Ind. Eng. Chem.*, 1919, **11**, 1145; *J.*, 1920, 111A.

[4] *J. Amer. Cer. Soc.*, 1920, **3**, 885; *J.*, 1921, 46A.

shrinkage, the water of plasticity, and the fineness of the clay grain, but decreases the apparent density. The use of caustic soda further increases the fineness of the grain of the clay. The strength of the clays after burning is increased from 127 to 1700% by the treatments mentioned.

L. Bertrand and A. Languine,[5] from a petrographic study of numerous clays, concluded that mica does not form the source of alkalis in clay, as has been frequently stated. There appears to be no definite relationship between the plasticity of a clay and its relative proportions of alumina and silica. Certain extremely "fat" clays owe their property to the colloidal state of their free silica or its presence in the form of very fine grains of quartz. A high alumina content does not necessarily guarantee a highly refractory nature, and, generally, the chemical composition offers no real clue to the ceramic value of a clay. Another point of view is outlined by J. S. Devereux,[6] who considers that resistance to high temperature is largely a question of physical chemistry, involving the application of the phase rule and the laws of solution. The various formulæ given in text-books for calculating the softening point of a mixture from its components appear, in his opinion, to have been formulated without any due attention to physico-chemical laws. L. Bertrand[7] further emphasises the necessity for petrographic investigation together with chemical analysis and states that from further work still to be published, he finds that various generally accepted ceramic axioms will not hold when subjected to microscopic investigation. Free silica, for example, is generally attributed to fine grains of quartz, but the author finds that certain clays which, by analysis, contain much free silica show very few quartz grains under the microscope. Further research proved the presence of hydrated silica even up to 18%, soluble in alkalis, and not polarised under the microscope. The author also deals in detail with the nature of plasticity as revealed by the microscope.

Experiments are described by J. Alexander[8] which concern the collating of the properties of clays with the size of their particles and the activity of motion of the colloidal matter. The author observes that the comparative freedom of the English kaolin from large particles (about 0·025 mm. diameter) demonstrates the care with which the washing and flotation are accomplished. The activity of the colloidal motion indicates absence of coagulating agents, and perhaps addition of deflocculators, either intentionally or in the local water used.

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[5] *Comptes rend.*, 1919, **169**, 1171 ; *J.*, 1920, 110A.

[6] *Chem. News*, 1920, **120**, 235.

[7] *La Céramique*, 1920, **23**, 50.

[8] *J. Amer. Cer. Soc.*, 1920, **3**, 612 ; *J.*, 1920, 628A.

[9] *J. Soc. Glass Tech.*, 1919, **3**, 201 ; *J.*, 1920, 408A.

Turning to physical properties, several papers are particularly interesting. H. J. Hodsman and J. W. Cobb[9] have determined the reversible expansion of certain materials, and they describe their apparatus. Great differences are found in the results given by the various refractories when heated up to 1000° C. Such materials as magnesia brick, carborundum, calcined alumina, calcined kaolin, and hard calcined ball clay expand regularly. With silica the inversion of α- to β-quartz causes a large expansion between 500° and 600° C., but from 600° to 1000° this is succeeded by a period practically without change. The same effect is noticeable in burned fireclay containing free silica. Glass pot mixtures do not vary greatly from the fireclays, but it is evident that pots made from kaolin, ball-clay mixtures, or from clays containing no free quartz, will be quite different from fireclay pots as regards their behaviour on heating and cooling, the latter type being particularly sensitive between 500° and 600° C. The contraction on cooling just below 600° of clay and silica exceeds the expansion found on heating. L. Bradshaw and W. Emery[10] have determined the specific heats of certain refractories between 25° and 1000°, 1200° and 1400° C., and find that all the materials examined, including silica, firebrick, and zirconia, have much greater specific heats at high temperatures than at ordinary temperatures.

Melting point methods at high temperatures are discussed by L. I. Dana and P. D. Foote,[11] and the melting points of a number of refractories are given. Above 1550° C. the use of optical pyrometers is necessary. Seger cones, which are useful under slow heating conditions, are not much use for the comparatively rapid heating rates used in the laboratory. The Arsem vacuum furnace is the type recommended, particularly since it is easily controlled even at 2500° C. and is free from smoke.

The load behaviour of refractories continues to attract attention. A. S. Watts[12] discusses the failure, under load at high temperatures, displayed by fireclay refractories, and quotes the opinions and results of a number of authors. Watts is led to enquire whether the failure of clay refractories high in alumina cannot really be attributed to a period of physical weakness produced in the mass by the decomposition of the kaolin and the recombination of the alumina and silica as sillimanite, and he produces evidence in favour of this view without making a definite pronouncement on the matter. Results of tests obtained by A. V. Bleininger[13] on the load behaviour of aluminous refractories indicate that highly aluminous refractories can be produced which are practically constant in volume and also resist load conditions. The main requirement is sufficiently high-firing temperature, and the author ascribes the failure of bauxite refractories to too low a temperature both when calcining the raw material and firing the bricks.

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[10] *Gas J.*, 1920, **150**, 579 ; *J.*, 1920, 518A.

[11] *Chem. and Met. Eng.*, 1920, **22**, 23, 63 ; *J.*, 1920, 175A, 208A.

[12] *J. Amer. Cer. Soc.*, 1920, **3**, 448 ; *J.*, 1920, 589A.

[13] *Ibid.*, 1920, **3**, 155 ; *J.*, 1920, 408A.

The purification of clays has also received well-merited consideration. The methods used for certain elutriation tests on kaolins are described by H. G. Schurecht[14] and results tabulated. F. Singer,[15] dealing with the electro-osmotic process as applied to kaolins concludes that this process is very markedly superior for purification to the older gravity methods which did not remove the finer impurities. J. S. Highfield, W. R. Ormandy, and D. Northall-Laurie[16] make particular reference to the commercial application of the principles of electrical osmosis to the purification of clays and similar materials and confirm Singer's views just quoted. The clay leaves the machine in the form of a blanket ¼–½ in. thick, containing only 25% of water and in a form which readily admits of drying. With osmosed clays sintering occurs at lower temperatures than with raw clays, thus saving fuel. The lower sintering temperature and higher melting point result in articles showing little further contraction after burning. The reduction of the sintering temperature is stated to be as much as 300° C. for low-grade clays, whilst bricks from some clays after osmosis are better burnt at 1100° C. than from the raw clays at 1300° C. Some of the aspects of colloid chemistry which have a bearing upon the technology of clays are presented by A. V. Bleininger.[17] The dispersed state of the finely-divided hydrated aluminium silicates, chiefly $Al_2O_3,2SiO_2,2H_2O$, imparts the property of plasticity. Kaolinite, the pure type mineral, rarely occurs in clays, but has usually been reduced to particles of the magnitude of 5μ or smaller, mixed with colloidal material like ferric oxide and organic matter, and often stained by absorbed salts. A clay is said to be plastic when the colloid matter is in excess, but non-plastic if the granular matter predominates. The colloid characteristics are substantiated by ultramicroscopic examination, and the work of J. Alexander[18] shows that the Brownian movement is observed with practically every type of clay suspended in water. This movement varies from the rapid motion of the finer particles to the more sluggish motion of the larger particles or aggregates, or when hampered by the presence of electrolytes. The author goes on to deal in detail with the effect of various reagents both electrolytes and non-electrolytes, on clay suspensions, and illustrates the points by reference to the purification of kaolins, to the so-called casting process and to the electro-deposition of the clay particles. The plasticity of clay is greatly affected by the presence of organic matter and the ageing of clays improves their plastic working property. It is thought that this is partly due to the formation of organic acids caused by bacterial action or chemical processes. The effect of colloids and electrolytes on the drying shrinkage and the firing of clays is also dealt with. Wherever the chemical composition and heat treatment permit it, the end result is the partial elimination of the colloid phases and their replacement by crystalline entities.

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[14] *Ibid.*, 1920, **3**, 355; *J.*, 19[illegible] 572A.

[15] *Berichte der Technisch-wissenschaftlichen Abteilung des Verbandes Keramischer Gewerke in Deutschland*, 1919, **5**, 16.

[16] *J. Roy. Soc. Arts*, 1920, **68**, 514.

[17] *J. Ind. Eng. Chem.*, 1920, **12**, 436.

[18] *Loc. cit.*

J. S. Laird and R. F. Geller[19] state that clays calcined at temperatures from 600° to 700° C. may be rehydrated and their plasticity largely renewed by treatment in the autoclave with water at 200° to 250° C. for 8 to 48 hours. Clays calcined at higher temperatures also become rehydrated under similar treatment but the change takes place much more slowly and is not nearly so complete. The authors suggest that the comparatively easy rehydration of clays calcined at the lower temperatures points to the formation of an anhydride during calcination, and this is broken down at higher temperatures and sillimanite is formed.

Dealing with the constitutional formulæ of kaolinite and other silicates, R. Wegscheider[20] considers that the constitution of polysilicates is such that the silicon atoms are never directly combined, but always combined through the oxygen.

SILICA REFRACTORIES.

The factors affecting the quality of silica refractories are discussed by D. W. Ross.[21] The specific gravity of silica bricks, usually between 2·65 and 2·27, indicates the degree of firing to which the bricks have been subjected. Minimum porosity can be obtained by raising the temperature as usual to 1250° C. or 1350° C. and keeping the bricks at that temperature for several days; the temperature should finally reach cone 18–20. The author also deals with the thermal volume changes and suggests certain standards for tests on silica refractories The volume changes, due to the inversion of quartz at high temperature, are also dealt with by L. Maddalen[22] although he applies his investigations to firebricks. To obtain the most satisfactory bricks, the author suggests that the complete conversion is required of free silica into stable silicates of iron, calcium, and aluminium, and of the residue to tridymite.

Comparative tests made by W. Emery and L. Bradshaw[23] show that there is no difference in porosity, refractoriness, refractoriness under load, reversible expansion to 1200° C., and after-expansion on heating to 1350° C. between hand-made and machine-made silica bricks. The machine-made bricks had a better shape, 28% greater crushing strength, and withstood the abrasive action of a sand blast better than hand-made bricks, whilst spalling was distinctly greater with hand-made bricks. Properly made, bricks produced by machine were the equal in all respects of hand-made bricks, and moreover, superior in certain ways.

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[19] *J. Amer. Cer. Soc.*, 1919, **2**, 828; *J.*, 1920, 24A.

[20] *Z. Elektrochem.*, 1919, **25**, 352; *J.*, 1920, 19A.

[21] *U.S. Bur. Standards, Tech. Paper* 116, 1919.

[22] *Revista Tecnica delle Ferrovie Italiane*, April 25, 1920.

[23] *Gas J.*, 1920, **150**, 577; *J.*, 1920, 518A.

F. Wernicke[24] states that it is not necessary to convert quartz completely to tridymite in bricks, provided that the maximum expansion is attained.[25] Using glacial quartzites for the manufacture of the bricks, complete expansion is obtained by one firing to 1450° and without prolonging the heating. Carboniferous types need two or three firings whilst felsquartzites expand even after several firings of long duration. Examined under the microscope, quartzites suitable for use in making bricks, contain minute crystals in a glassy matrix. Large crystals, or portions of large crystals, indicate unsuitability. Tertiary quartzites are suitable for the manufacture of bricks for the arches of metallurgical and electric furnaces and carboniferous quartzites are better for glass furnaces, regenerators, and coke-ovens.

Two very similar papers appear dealing with diatomaceous earth. A. Bigot[26] finds that infusorial earth of this type is a much more effective heat insulator than silica or fireclay bricks, and quotes certain furnace test results in support of this. W. Phalen[27] also recommends it for covering boilers, steam pipes, furnaces, and stoves, and for fireproof cements. Both authors give a number of analyses of samples of kieselguhr.

Glass Refractory Materials, Pots, Tankblocks, Etc.

The Bureau of Standards (U.S.A.)[28] has commenced an investigation with the object of improving refractories for the glass industry, especially as regards their resistance to corrosion. It is proposed to treat the mattersy stematically, and a large number of crucibles have been made from such mixtures as silicious bond clays with aluminous grog and aluminous bond clays with silicious grog. These crucibles, after being subjected to the action of a corrosive barium glass, will be broken up and a measure of the attack obtained. Shrinkage and transverse strength of the mixtures will also be measured.

The necessity for fundamental research into the refractories question is fully recognised in this country and E. M. Firth, F. W. Hodkin, and W. E. S. Turner[29] publish an account of tests made on

[24] *Stahl u. Eisen*, 1920, **40**, 432; *J.*, 1920, 408A.

[25] *Cf.* L. Maddalen, *loc. cit.*

[26] *La Céramique*, 1920, **23**, 79.

[27] *British Clayworker*, 1920-1921, **29**, 148.

[28] *U.S. Bur. Standards, Tech. News Bull.* 40, 1920.

[29] *J. Soc. Glass Tech.*, 1920, **4**, 162; *J.*, 1920, 628A.

twenty-seven British clays. These tests include chemical composition, drying and firing shrinkage, porosity and density, the physical tests being applied to samples fired at various temperatures up to and including 1400°. Calculated rational composition is of no apparent value as regards the relationship between the mineral constitution and properties of the clays, whilst the ultimate composition gave no clue as to the plasticity of clays or the amount of water required to render the clay plastic.[30] The aluminous clays were, however, generally more difficult to work than the silicious types, and showed a wider porosity range. Tables of figures and diagrams are given relating to all the clays examined. In a subsequent paper the same authors[31] deal in similar fashion with china clay.

The effect of added felspar on the shrinkage and porosity of aluminous fireclays is described by E. M. Firth and W. E. S. Turner.[32] The addition of felspar as a flux diminishes the shrinkage up to a temperature of about 1000° or 1100° and, in general, makes the change in shrinkage more uniform. Increasing amounts of felspar bring about a considerable reduction of porosity at temperatures exceeding 1100°–1200° C.

J. Baldermann[33] states that grog for glass furnace refractories should never be greater than 3 mm. in diameter and should be fired until no further shrinkage occurs. Addition of coarse quartz was useless. Old pots are excellent for use as grog.

M. W. Travers[34] suggests that the ideal refractory consists of a system of interlocking crystals formed *in situ* in a glassy matrix. If the matrix is such as to form a sillimanite layer in contact with alkaline fluxes, then corrosion by glass is largely avoided. The Malinite process for the production of sillimanite refractories is described by A. Malinovszky,[35] the aluminous rock or mineral being smelted with a reducing agent in a cupola furnace of special design. The fused mass obtained is highly refractory, free from expansion and contraction at any temperature and does not warp, crack, or spall on change of temperature. Heated in an electric furnace in contact with carbon resister plates at a temperature of about 1650°, malinite brick is unaffected. The author gives a detailed account of the examination of the product.

The production of pots for glass making is receiving considerable attention, the casting process in particular being the subject of several investigations. J. W. Wright and D. H. Fuller[36] consider the casting of porcelain glass pots. The characteristics of a casting slip and also of the fired body depend on composition, size of grog, and upon the peculiar physical and chemical qualities inherent in primary kaolins as differentiated from secondary ones and in ball clays against fireclays; they further depend on the amounts of sodium carbonate and sodium silicate used. All these factors are considered in detail and successful mixtures given.

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[30] *Cf.* L. Bertrand and A. Languine, *loc. cit.*

[31] *J. Soc. Glass Tech.*, 1920, **4**, 264 ; *J.*, 1920, 820A.

[32] *Ibid.*, 1920, **4**, 392.

[33] *Tonind. Zeit.*, 1920, **44**, 581, 612.

[34] *J. Soc. Glass Tech.*, 1920, **4**, 138 ; *J.*, 1920, 628A.

[35] *J. Amer. Cer. Soc.*, 1920, **3**, 40 ; *J.*, 1920, 365A.

[36] *Ibid.*, 1919, **2**, 659 ; *J.*, 1919, 766A.

The effect of the method of preparation on the viscosity of a casting slip has been examined by V. S. Schory.[37] Blunging, screening, and filter-pressing together with the same portions of body, water, sodium carbonate, and sodium silicate were used. Of the slips prepared by blunging, those with the lowest alkaline reagent content give the firmest casts. The methods of preparation requiring the greater amount of sodium salts to bring the slips to their best casting condition give the softer casts. A. B. Taylor[38] deals with the preparation of casting slip and a method of casting pots for use in experimental work on optical glasses. The results obtained are indicated and examination of the grog distribution by microscopic means is described.

An improved method of manufacture for glasshouse pots is suggested by C. W. Thomas,[39] a covered pot being made in two sections in order that the interior surface of the pot may be worked up when in a hard and toughened condition. To prevent anything in the nature of an open joint, an asbestos cushion joint is used.

S. R. Scholes[40] describes a process which entails the use of 5–10% of felspar with 90% of the ordinary clay batch as the mixture for the inner surface of glass pots. This mixture gives a dense body after burning at 1300° C. and shows no sign of overfiring. The felspar forms a sintering bond between the clay particles, producing the phenomenon generally referred to as vitrification. The lining, which is applied during the pot-making in the ordinary way, so as to give a finger course about ½ in. thick up to the metal line and in gradually diminishing thickness for 8 inches above that, is very dense, formation of stones is reduced to a minimum, and the useful life of the lined pot is from two to three times that of the ordinary pot for lead-potash melts. The later paper by E. M. Firth and W. E. S. Turner[41] provides definite experimental data, furnishing evidence in support of the idea underlying Scholes' process.

REFRACTORIES FOR THE IRON AND STEEL INDUSTRIES.

C. E. Nesbitt and M. L. Bell[42] state that the most important working qualities of silica brick can be determined by spalling and hot crushing tests and those of fireclay bricks by these two tests and

[37] *J. Amer. Cer. Soc.*, 1920, **3**, 286; *J.*, 1920, 546A.
[38] *J. Soc. Glass Tech.*, 1920, **4**, 140; *J.*, 1920, 627A.
[39] *J. Soc. Glass Tech.*, 1920, **4**, 107.
[40] *J. Amer. Cer. Soc.*, 1920, **3**, 498; *J.*, 1920, 598A.
[41] *Loc. cit.*
[42] *J. Ind. Eng. Chem.*, 1919, **11**, 1149; *J.*, 1920, 111A.

a slagging test. Silica bricks show a fall in crushing strength when heated to 1350° C. and the finer the material of which they are made, the greater the spalling loss and the shorter the life in the furnace. Three standard methods[43] are given for tests on the penetrative action of slags on fireclays and firebricks, including the method used by Nesbitt and Bell.[44]

A compilation of the chief information published on the occurrence, properties, and uses of magnesia as a refractory is presented by J. S. McDowell and R. M. Howe.[45] Particulars are given of the specific gravity, porosity, crushing strength, specific heat, thermal conductivity, electrical resistivity, and linear expansion under load. Microscopical examination reveals the formation of magnesioferrite in dead-burned magnesia but the main action of the iron oxide is catalytic, hastening the formation of periclase.

Dealing with the question of refractories for electric furnaces, insulators, etc., R. C. Purdy[46] argues that most new requirements as regards refractory materials will be met by intelligent adaptation of materials in general use, probably by fusing them so that they attain complete chemical stability and constancy in volume. The report of a symposium on refractories for electric furnaces[47] confirms Purdy's statement, and indicates that the refractory materials from which choice is likely to be made are alundum, spinels, sillimanite, and zirconia.

Other Refractories.

The report of an investigation into the properties of refractory materials used in coke-oven construction is published by W. C. Hancock.[48] The scheme adopted is the examination of specimens of coke-oven linings which have proved satisfactory in use and then the investigation of selected raw refractory materials of British origin likely to be of service. The special qualities required for materials for coke-oven construction are enumerated and full details are given of chemical composition, mechanical properties, texture, abrasion, porosity, density, permeability, expansion, and the action of salty coals. The salts mainly responsible for action on coke-oven linings are sodium chloride and sodium sulphate, but these salts are partially removable from coal by washing. The result of coal washing and flux tests are reported. Another factor in the destruction of oven linings appears to be the deposition of carbon in the pores of the refractory material, arising from decomposition of methane or other hydrocarbons.

L. P. Ross[49] ascribes the failure of certain blast-furnace stock-line bricks to the deposition of carbon, but in this case produced from carbon monoxide in the gas used as fuel by the action of iron oxide in the bricks.

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[43] *Trans. Cer. Soc.*, 1918-1919, **18**, 516 ; *J.*, 1920, 234A.
[44] *Loc. cit.*
[45] *J. Amer. Cer. Soc.*, 1920, **3**, 185 ; *J.*, 1920, 490A.
[46] *J. Ind. Eng. Chem.*, 1919, **11**, 1151 ; *J.*, 1920, 111A.
[47] *Chem. and Met. Eng.*, 1920, **23**, 769.
[48] *Iron and Steel Inst., Carnegie Schol. Mems.*, 1920, **10**, 41 ; *J.*, 1921, 116A.
[49] *Iron Age*, 1920, **2**, 117.

Silica refractories, according to W. J. Rees,[50] can now be manufactured with physical properties such as will make their successful use in coke oven practice a distinct possibility. This is accomplished by combining the two factors of suitable grading and adequate burning. The same author in a further paper[51] confirms the corrosion of bricks by soluble salts in coal, particularly sodium sulphate and chloride,[52] and considers the actions occurring in detail. Corrosion by salt is more severe on fireclay than on silica bricks, partly as a result of direct action and partly due to the fireclay bricks shrinking in use and so causing open joints which expose a greater area to attack. A suitable natural or artificial mixture of silica and firebrick may be obtained and will produce bricks which neither shrink nor expand. Reference is also made to the deposition of carbon in the pores of the bricks with the resultant production of the fusible ferrous silicate. H. V. Thompson[53] states that highly aluminous clays burnt so as to develop a large proportion of sillimanite are much more resistant to the action of salt than ordinary fireclay, this statement agreeing with a similar one by Rees.[54]

Turning to specialised refractories, M. L. Hartmann, A. P. Sullivan, and D. E. Allen[55] have determined the electrical resistivity at high temperatures of nine different commercial refractories. Bauxite bricks, silica bricks with lime bond, coarse texture fireclay bricks of grade A quality, crystallised carborundum (refrax) bricks, and carborundum bricks containing 95% of "carbofrax C" give regular resistivity curves. The last mentioned bricks show a constant resistivity when held at a temperature of 1500° C., whilst "carbofrax B" show a rapid decrease of resistivity with increasing time of heating. Magnesia bricks give a marked difference between the curves during heating and cooling and further show a constant resistivity between 1000° and 1150° C. The authors consider this indicative of a change in the physical structure of the magnesia. This peculiarity in the case of magnesia is only shown in the heating curve. Marked difference is found between the heating and cooling resistivity curves of natural zirconia with a permanent change shown on heating zirconia to 1200° C. Chrome bricks show low resistivities at all temperatures. A comprehensive table of resistivities at temperatures up to 1500° C. is given. M. L.

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[50] *J.*, 1920, 197T.

[51] *Gas World*, 1920, 72, *Coking Sect.*, 9.

[52] *Cf.* W. C. Hancock, *loc. cit.*

[53] *Pottery Gazette*, 1920, 45, 770.

[54] *Loc. cit.*

[55] *Trans. Amer. Electrochem. Soc.*, 1920, 1 ; *J.*, 1920, 690A.

Hartmann and O. A. Hougen[56] find that the least spalling (0 to 12%) occurs with carborundum and high-grade fireclay bricks. Bauxite, zirconia, and low-grade fireclay bricks show spalling from 43 to 65%, whilst chrome, silica, and magnesia bricks are completely destroyed under similar conditions. Abrasion tests made by M. L. Hartmann and J. F. Kobler,[57] using a carborundum wheel for grinding under specified conditions, show very considerable variations in bricks of the same kind and even from the same manufacturer. Carborundum, zirconia, and bauxite bricks are most resistant and silica and higher grade firebricks least resistant at ordinary temperatures. At 1350° C. a very similar order is obtained with a notable exception in the case of magnesia, where the decrease in resistance is very great whilst silica brick spalled and tests could not be made.

H. E. Coley[58] states that up to the present no sufficiently cheap process has been devised to allow of the use of pure zirconia in refractory bricks. The problem of plasticity has been largely solved and the shrinkage can be influenced by the addition of grog in the form of previously fired and ground zirconia ; vitrified grog was a source of weakness. Zirconia bricks can be produced and fired having a melting point of not less than 2300° C., a low coefficient of expansion, a low conductivity, a resistance to slags better than that of other refractories, a capacity to resist very great pressures when cold and a greater pressure than other refractories when hot, and can be heated and cooled alternately and rapidly without deterioration. An account of various chemical processes for the preparation of zirconia, the preparation and properties of zirconium metal, and methods for analysis of zirconium ores is given by J. W. Marden and M. N. Rich[59] in a summary of a report issued by the U. S. Bureau of Mines. E. W. Washburn and E. E. Libman[60] have made an approximate determination of the melting point diagram of the system zirconia-silica, and the estimated "true" melting points of various mixtures are given. The results indicate that for use as a refractory up to 2550° C. the presence of silica as an impurity in zirconia is not necessarily detrimental, since the addition of silica up to a 33% total eliminates its fluxing action. Such a refractory will have the properties of zirconium silicate but will be nearly as resistant to high temperatures as pure zirconia. Refractories of considerable strength, it is suggested, could possibly be made from powdered zircon bonded with a mixture of zirconium hydroxide and silica in molecular proportions and fired in an electric furnace.

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[56] *Ibid.*, 1920, 349 ; *J.*, 1920, 365A.

[57] *Ibid.*, 1920, 355 ; *J.*, 1920, 365A.

[58] *Chem. News*, 1920, **120**, 7.

[59] *J. Ind. Eng. Chem.*, 1920, **12**, 651 ; *J.*, 1920, 596A.

[60] *J. Amer. Cer. Soc.*, 1920, **3**, 634 ; *J.*, 1920, 628A.

CERAMICS AND BUILDING MATERIALS.

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THOUGH many valuable papers bearing on these subjects have appeared, the volume of work published during the period under review has scarcely been as large as in the preceding year. This may be due in part to an accumulation of results, the publication of which was necessarily deferred till after the war, and possibly in part to the fact that many institutions which were temporarily engaged on various problems of national importance have now returned to their normal activities in education and training. It is, however, to be hoped that the channels of investigation which were opened up after 1914 will be kept open and extended in the future as a means of attaining improvements and more economical production during peace.

CERAMICS.

Clays etc.—R. Wegscheider[1] considers that in the constitutional formulæ of kaolinite and polysilicates, the silicon atoms should be represented as joined through an oxygen atom and not directly with one another. In the latter case, the compounds are reducing agents and are unstable. If the silicon atoms are united directly the oxygen atoms will be similarly united, a condition that also tends to instability. J. S. Laird and R. F. Geller[2] experimented with a view to re-hydrating calcined clays and found that those clays that had been dehydrated at a moderate temperature (600°–700° C.) could be re-hydrated, preferably after wet-grinding, by being heated in water, under pressure, to temperatures of 200°–270° C., for a sufficient length of time (8–48 hrs.). Clays that had been calcined at higher temperatures could only be re-hydrated much more slowly and incompletely. They suggest that on dehydration kaolinite forms an anhydride which can be re-hydrated, but is broken down on heating to higher temperatures owing to other reactions, such as the formation of sillimanite.

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[1] *Z. Elektrochem.*, 1919, **25**, 352 ; *J.*, 1920, 19A.

[2] *J. Amer. Cer. Soc.*, 1919, **2**, 828 ; *J.*, 1920, 24A.

L. Bertrand and A. Languine[3] consider from the petrographic study of a number of clays that the view that the alkalis present are in the form of mica is incorrect. The relative proportions of silica and alumina are not a definite guide as to whether a clay is " fat " or " lean," as many clays rich in the former are abnormally "fat " owing to the free silica being in a colloidal condition. In many cases also a high content of alumina was not accompanied by a high refractoriness, so that the chemical composition of a clay is not a criterion of its ceramic qualities. H. Chatley[4] has suggested the hypothesis that plasticity and the specific colloid properties of sub-divided matter, when the molecules of the fluid are also taken into account, are due to molecular forces comparable with weight or other external agency. P. Rona and P. György[5] found that nearly all of a number of organic electrolytes examined increase the velocity of sedimentation of kaolin. In homologous series the acceleration increases with the length of the chain and only compounds virtually insoluble in water exert no effect.

E. M. Firth, F. W. Hodkin, and W. E. S. Turner[6] found that a china clay of ordinary composition required 49·5% of water to bring it to a moulding consistency. On firing the colour changed from creamy white to a slight pink between 600° and 1100° C. but was dead white at 1200°. The fracture of pieces fired at 1400° showed a slight glaze which increased at 1500° and the colour became bluish white. The shrinkage remained below 5% up to 1000° and then rapidly rose to 22% at 1500°. The porosity was 50% at 600°, rose to a maximum of 56% at 900°, and then fell to 2·4% at 1500° C.

L. Bertrand and C. Boulanger[7] recommend the use of carbon tetrachloride in place of water for the determination of porosity of ceramic materials. Owing to the low surface tension of the tetrachloride a paving tile, for example, can be saturated in about one-thirtieth of the time that would be required if water were used. For accurate work the saturated test-piece should be weighed in a light metal vessel to avoid losses due to rapid evaporation. A. S. Watts[8] has pointed out that the ordinary classification of clays as " kaolins," " ball clays," etc. is often very misleading, and with regard to many properties there is considerable overlapping. He has proposed a system of classification based on the ceramic qualities of the clays and selected the five properties, colour, shrinkage, bonding power, vitrification, and fusion point, and each of these, except colour, is sub-divided into five groups, ranging from "low"

[3] *Comptes rend.*, 1919, **169**, 1171 ; *J.*, 1920, 110A.

[4] *Trans. Cer. Soc.*, 1919-20, **19**, 1.

[5] *Biochem. Zeits.*, 1920, **105**, 133 ; *J.*, 1920, 722A.

[6] *J. Soc. Glass Tech.*, 1920, **4**, 264 ; *J.*, 1920, 820A.

[7] *La Ceramique*, 1920, **23**, 77 ; *J.*, 1920, 658A.

[8] *J. Amer. Cer. Soc.*, 1920, **3**, 247 ; *J.*, 1920, 490A.

to "high," according to amount. H. G. Schurecht[9] has made a number of comparative elutriation tests of American kaolins and English china and ball clays, with a modified Schulze apparatus. The paper describes the technique of elutriation and points out that distilled water should be used instead of tap water, the dissolved salts of which favour coagulation of fine particles which then settle out as apparently larger grains. Deflocculation of the clays is secured by the use of appropriate amounts of caustic soda and the loss of this, during elutriation, is remedied by the introduction of dilute ammonia in the feed water. Kaolins from Georgia, South Carolina, and Pennsylvania compared favourably with English china clays and the great plasticity of ball clays is suggested as being due to the very high proportion of very fine grains.

W. R. Ormandy[10] gave a very interesting account of the electro-osmotic purification of clays, explaining the phenomena involved and the advantages that are obtained by the process in enhancing the qualities of the products. J. S. Highfield,[11] in conjunction with Ormandy and Northall-Laurie, dealt with the same subject mainly from the electrical standpoint, the lecture being illustrated by a number of well-chosen experiments and extremely fine photomicrographs. J. Alexander[12] has subjected a number of clays to ultra-microscopic examination and discussed the relationship between the characters thus revealed and the working properties of clays, regarding the whole question from a colloid-chemical standpoint. Many clays, *e.g.*, English china clay, contain many actively colloidal particles, and several contain iron salts and other diffusible products of the hydrolysis of clays which probably balance the deflocculating effect of the organic substances present. This paper also suggests a reference to one by A. B. Peck[13] on the application of the polarising microscope to ceramics, which, though a very specialised study, has already afforded much information as to the nature of silica bricks, Portland cement, etc., and is likely to play an increasingly important *rôle* in future investigations.

Bodies etc.—F. H. Riddle[14] has investigated the effects produced in the manufacture and on the properties of porcelain by the introduction of small quantities of lime and magnesia, which, as is well known, reduce the temperature at which such bodies mature. Incidentally, it was found that fine grinding also caused earlier maturity and earlier overfiring. As magnesia lowers the temperature at which ceramic bodies mature, A. Berge[15] investigated its use with the view of saving fuel, and concludes that it can be employed satisfactorily with that result. Riddle[16] also investigated the relation of chemical composition to thermal expansion of porcelain. Bodies with a high clay content showed a low thermal expansion. Variations of the content of flint, which naturally can only be small in such bodies, showed no decided lowering of the expansivity, but replacement of flint by calcined kaolin, sillimanite, etc. has the effect of decreasing thermal expansion. J. W. Mellor[17] contributes a valuable paper on the composition and the chemical changes occurring in bone china bodies. R. L. Johnson[18] deals with the question of grinding in pan or cylinder mills ; equally good bodies and ware can be made with either, but the cost of grinding a good quality flint to a fine degree is more in the former than in the latter. He also deals with other points in the preparation of earthenware bodies, the plasticity of which must be developed as fully as possible. N. B. Davis[19] advocates the use of apatite in place of bone ash in bone china bodies as it is cheaper, but it was pointed out in the discussion on his paper that although excellent results are obtained with articles of simple form, difficulties are encountered on the manufacturing scale, due to deformation etc. H. V. Thompson[20] found that of the four lead borates enumerated by Abegg, only the triborate and the metaborate have definite chemical compositions.

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[9] *Ibid.*, 1920, **3**, 355 ; *J.*, 1920, 572A.

[10] *Trans. Cer. Soc.*, 1918-19, **18**, 327 ; *J.*, 1920, 234A.

[11] *J. Roy. Soc. Arts*, **68**, 514.

[12] *J. Amer. Cer. Soc.*, 1920, **3**, 612 ; *J.*, 1920, 628A.

[13] *Ibid.*, 1919, **2**, 695.

[14] *Ibid.*, 1919, **2**, 812 ; *J.*, 1920, 24A.

[15] *Sprechsaal*, 1920, **53**, 1, 9 ; *J.*, 1920, 296A.

In addition to the paper by Berge, already referred to, the necessity of economising fuel in Germany is also suggested by a paper by T. Hertwig,[21] who considers that in future porcelains maturing at cone 7–9 will be extensively used. He asserts that all German hard porcelains may be biscuit fired at cone 9, when finely ground, though if the grinding is too fine the glaze is apt to craze. In the soft French porcelains the ratio of clay to quartz is less important than in the harder German product, and the slight bluish tinge in porcelains fired at cone 7–9 when quartz is used disappears, according to Hertwig, when flint is substituted. R. L. Clare and F. Albery[22] have investigated the effect of variation in the size of grog used in terra cotta bodies. The results obtained show that the grog must be carefully controlled in order to secure uniformity in the finished ware, and the authors suggest that instead of grog being obtained haphazard, it would probably be worth the extra cost if it were prepared at some central plant, from which a terra cotta manufacturer could obtain a supply of uniform material most suited to his particular needs. Whether such a scheme would be applicable in this country might be worth consideration. H. E. Davis[23] has also investigated the size of grain of grog and concludes that in order to ensure good strength in both the green and fired ware, the grog should contain rather a large amount of fine material, *i.e.*, roughly up to about 0·4 mm. diameter in these trials. Fine material is also desirable in such bodies if they are to be slip-coated, as with it a close-fitting smooth-surfaced coating can be obtained. H. Wilson[24] in a study of terra cotta slips emphasises the view that the grain size and the proportioning of grog sizes are of great importance in securing satisfactory vitreous slips. Apart from the composition of the slip, the shape of the particles is of importance and would, according to the author, include a study of magnesium and magnesium-aluminium silicates, as represented by asbestos, steatite, etc. M. E. Gates[25] advocates the use of barium hydroxide in place of the carbonate for the prevention of scum on terra cotta bodies and describes a mechanical device for supplying the solution in manufacture.

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[16] *J. Amer. Cer. Soc.*, 1919, **2**, 804 ; *J.*, 1920, 24A.

[17] *Trans. Cer. Soc.*, 1918-19, **18**, 497 ; *J.*, 1920, 235A.

[18] *Ibid.*, 1918-19, **18**, 321 ; *J.*, 1920, 234A.

[19] *Ibid.*, 1918-19, **18**, 378 ; *J.*, 1920, 235A.

[20] *Ibid.*, 1918-19, **18**, 510 ; *J.*, 1920, 235A.

[21] *Sprechsaal*, 1920, **53**, 363 ; *J.*, 1920, 690A.

[22] *J. Amer. Cer. Soc.*, 1920, **3**, 384 ; *J.*, 1920, 572A.

A. Heath and A. Leese[26] have studied the effect of lime in earthenware bodies. They review some of the earlier papers on the subject, and from their own experiments they are of opinion that satisfactory results can be obtained both as regards body and glaze, even when lime replaces Cornish stone wholly. H. S. Newman[27] has continued his previous work on the contraction of mixtures of ball clay, china clay, stone, and flint. He finds that when fired to cone 016, most of the test-pieces showed an expansion beyond the dry length. When the ratio of stone to flint falls below 3 : 2, the replacement of ball clay by china clay increases the contraction, but when that ratio is passed the reverse action takes place at cone 1*a* and at cones 6*a* and 8 the ratio of stone to flint must be below 2 : 3 before this reverse action occurs. The maximum contraction occurred with a mixture that contained no ball clay. B. J. Allen[28] has given a valuable account of the casting of heavy ware and the use of pressure and vacuum in the process. V. S. Schory[29] has shown that the viscosity of a slip may vary according to the method of its preparation. Blunged slips with the lowest alkali content give the firmest casts as alkali may cause many troubles with the moulds and also with the dried and fired wares. A. Granger[30] gives a short historical survey of the development of the tunnel kiln. I. E

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[23] *Ibid.*, 1920, **3**, 641 ; *J.*, 1920, 628A.

[24] *Ibid.*, 1920, **3**, 114 ; *J.*, 1920, 408A.

[25] *Ibid.*, 1920, **3**, 313 ; *J.*, 1920, 546A.

[26] *Trans. Cer. Soc.*, 1919-20, **19**, 93.

[27] *Ibid.*, 1919-20, **19**, 132.

[28] *Ibid.*, 1918-19, **18**, 363.

[29] *J. Amer. Cer. Soc.*, 1920, **3**, 286 ; *J.*, 1920, 546A.

[30] *Trans. Cer. Soc.*, 1919-20, **19**, 110.

Sproat and D. Allbright[31] give their experience of working a Dressler tunnel oven, and pay a high tribute to its efficiency, both as regards the uniformity of the products and the reduction effected in the cost of firing. C. B. Harrop[32] briefly reviews the advantages of tunnel kilns, which are also regarded from a rather different point of view by S. Trood,[33] and G. Brain[34] describes the working of the first of these ovens installed in America. In connexion with processes of manufacture, H. Spurrier[35] contributes an interesting paper on pug mill control, in which he points out that pugging tends to cause segregation of flint and spar, forcing them through the plastic clay towards the wall of the mill. He has devised an apparatus for determining the pressure in pug mills and studied the distribution of occluded air in a plastic body. L. G. Hill,[36] supplementing a paper read in 1914, recommends the Griffin mill in place of a ball mill, and also lays stress on the advantages of obtaining angular particles as a result of grinding. B. J. Allen[37] gives an interesting paper on the drying of ceramic articles, especially keeping in view the control of humidity and temperature, and their importance in drying generally.

A. W. S. Odelberg[38] contributes a useful paper on some new appliances in potting, which include electrical railways for drawing ovens, the jolleying of square dishes, plate making machinery, and also the employment of elutriation for controlling the fineness of ground materials.

Glazes and Enamels.—L. Petrik[39] gives some notes on lead glazes, with a lead solubility of less than 1%, and leadless frits, and suggests that standard frits could be prepared on a large scale at lead works more cheaply than by the potters themselves. G. Heinstein[40] states that the yellow colour of glazes containing lead, alumina, and silica which are unsuitable for ivory and white ware, may be overcome by replacing, say 0·25 equivalent of lead oxide (or more if boric acid is present) by any other metallic oxide such as zinc or magnesium oxide. E. C. Hill,[41] in experiments on Bristol glazes, finds that tin oxide increases the whiteness, but if more than 7% is present it causes crawling and cracks. Tin oxide and barium carbonate reduce the fusibility of a glaze, and magnesium oxide also makes it more refractory. From a series of experiments, R. H. Minton[42] finds that zinc oxide is useful in terra cotta and porcelain glazes. Stannic oxide and barium oxide increase the opacity more than clay, and arsenic oxide is nearly as efficient as stannic oxide. Zirconium oxide is perhaps the best substitute for stannic oxide, but its employment would have to depend on the price. G. Blumenthal[43] concludes that the slight solubility in water shown by a number of commercial boric acid frits is due to the fact that they have not been completely melted.

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[31] *J. Amer. Cer. Soc.*, 1920, **3**, 460.
[32] *Ibid.*, 1920, **3**, 697.
[33] *Ibid.*, 1920, **3**, 701.
[34] *Ibid.*, 1920, **3**, 706.
[35] *Ibid.*, 1920, **3**, 388.
[36] *Trans. Cer. Soc.*, 1919-20, **19**, 3.
[37] *Ibid.*, 1919-20, **19**, 26.
[38] *Trans. Cer. Soc.*, 1919-20, **19**, 42.
[39] *Sprechsaal*, 1920, **53**, 405; *J.*, 1920, 722A.
[40] *Ibid.*, 1920, **53**, 31, 44; *J.*, 1920, 296A.
[41] *J. Amer. Cer. Soc.*, 1920, **3**, 13; *J.*, 1920, 296A.

J. D. Whitmer[44] has investigated the production of bluish and greenish-grey colours in glazes by the use of nickel and magnesium oxides. R. Berg[45] found that a glaze that had been in use for earthenware when applied to wall tiles showed "blinding" or devitrification especially near the edges. The defect was found to be due to absorption of part of the glaze by the body, and was remedied by increasing the viscosity of the glaze by adding zinc oxide. The slight opacity produced could be overcome by increasing the proportion of lime and potash or the total RO oxides. F. B. Ortman[46] has studied the composition of kiln gases and their effect on terra cotta glazes. Sulphur is perhaps the worst enemy in the gases, and the author concludes that the utmost ventilation of the kiln and flues must be maintained consistent with attainment of sufficient heating effect. R. R. Danielson[47] recommends, in addition to the usual methods of cleansing sheet iron and steel before enamelling, the employment of boiling solutions of sodium hydroxide or carbonate, especially with the aid of an electric current, in order to remove grease. Solvents such as naphtha etc. are not suitable, as they leave a thin film of grease on the sheet. For heavy sheets sand-blasting can be used. Electrolytic pickling in dilute sulphuric acid is said to be quicker and cheaper than simple acid pickling, and the sheets should always be rinsed with alkali to ensure neutralisation of any acid and immediately dried at 150°–230° C. J. B. Shaw[48] has examined a defect in enamelled ware known as "fish-scaling," which consists of small pits formed by specks of the ground-coat enamel jumping off. It is distinct from blistering, due to impurities rolled into the steel, and from pitting, due to rusting of the metal. The author believes that the defect is chiefly due to the preparation, application, and burning of the enamel, which should not contain too large an amount of finely ground material. C. Treischel[49] has called attention to a form of blistering in which the enamel splits off in aggregates of small blisters or in rows or striations. He considers it due to hydrogen liberated from sheets that have been pickled in 10% hydrochloric acid. If the strength of the acid is reduced to 3% no blistering occurs, and the sheets should be brushed before washing in order to remove the scale. Further work on the action of acids on enamels has been published,[50] the acid in this case being citric, and it is found that the extent of the action of the acid is very nearly related to the discoloration produced on the etched portions of the vessels when treated with a dilute solution of malachite green. R. D. Landrum and L. J. Frost[51] have experimented with enamels containing titanium oxide as an opacifying agent. An excess of the oxide prevents the enamel remaining in suspension properly and should not be used in a ground coat as it destroys the cobalt blue and lowers the melting point and affects the adhesion of the enamel.

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[42] *Ibid.*, 1920, **3**, 6 ; *J.*, 1920, 366A.
[43] *Ibid.*, 1920, **3**, 152, *J.*, 1920, 408A.
[44] *Ibid.*, 1920, **3**, 663 ; *J.*, 1920, 598A.
[45] *Sprechsaal*, 1920, **53**, 19 ; *J.*, 1920, 296A.
[46] *J. Amer. Cer. Soc.*, 1920, **3**, 476.
[47] *Ibid.*, 1919, **2**, 883 ; *J.*, 1920, 111A.
[48] *Ibid.*, 1920, **3**, 489 ; *J.*, 1920, 599A.
[49] *Ibid.*, 1919, **2**, 774 ; *J.*, 1920, 25A.

BUILDING MATERIALS.

Cements etc.—K. Endell[52] has examined the ternary system, CaO-SiO_2-Al_2O_3, to determine the limits within which compounds are formed that are capable of hydraulic setting. Good cement clinkers were found to contain the following compounds which have been identified mineralogically:—CaO,Al_2O_3, the group of orthosilicates $2CaO,SiO_2$, and $3CaO,5Al_2O_3$. The compounds $3CaO,Al_2O_3$ and $2CaO,Al_2O_3,SiO_2$, do not form cements, and it is also stated that the compressive strengths of the products depend on the alumina content. J. C. Witt[53] has critically surveyed the methods of determining the calcium carbonate in the raw materials for Portland cement and discussed the various errors due to the nature of the constituents, and to the different apparatus and methods adopted. As tricalcium aluminate and tricalcium silicate are responsible for the changes in Portland cement known as the initial and final set, A. J. Phillips[54] made a careful study of the behaviour of the amorphous aluminate with large and small quantities of water and in the presence of salts. He found that with large amounts of water the tricalcium aluminate formed a suspension containing small amounts of coarsely dispersed and molecularly dispersed material. It is coagulated not by heat but by freezing and has a great capacity for the adsorption of ions and undissociated salts and resembles the sols formed from Fe_2O_3, Al_2O_3, and Cr_2O_3. With smaller amounts of water, comparable with those used in cement pastes, the aluminate is converted into and remains a gel at least during the first 24 hours after mixing. R. Nacken[55] has found that in making Portland cement from Rüdersdorf raw materials a strong exothermic reaction occurs between 1200° and 1300° C. followed by an endothermic reaction which accompanies sintering. With pure materials free from MgO, SO_3, etc. the exothermic reaction is most strongly marked at 1350° C. F. Killig[56] determined by a calorimeter the heat evolved during the setting of cement; judging from a number of samples tested this determination appears to be more satisfactory for the purpose than the use of the Vicat needle. J. Bahmann[57] has called attention to the fact that when calcium cyanamide is decomposed into calcium carbonate and ammonia a sludge is left in the autoclave which consists largely of lime and free carbon, and has a high loss on ignition. When this is mixed with the calculated amount of dry clay and calcined to a white heat, it yields a cement with the properties and approximate composition of Portland cement. J. C. Witt[58] made additions of gypsum to cement and also to clinker and noted how the physical properties, notably the time of setting, were affected by the alteration in the amount of SO_3. When the gypsum was added to the cement the time of setting appeared to be unaffected by the SO_3 content, but in the case of the addition to the clinker the results were very irregular. Exposure of the cement to air was also very variable and was independent of the SO_3 content. Addition of lime up to 2% to a cement with an SO_3 content of about 2% increased the time of setting, but this was independent of the SO_3 content. A. Guttmann[59] found that addition of raw gypsum or calcium chloride caused Portland, iron-Portland, and blast-furnace cements to swell, so that the natural shrinkage is masked, or only occurs after a long time. D. A. Abrams[60] has recorded a number of experiments on the effect of fineness of cement on the qualities of the concrete made from it. Briefly, for a given cement, the strength of the concrete increased with the fineness, for all proportions of the mixture, for all consistencies of the wet mixture, qualities of the aggregate and ages of the concrete, but these qualities vary with different cements. Fineness has a greater effect on the strength of concrete when a small proportion of cement is used, but the effect decreases with the age of the concrete. The density of the concrete and its expansion or contraction under water or in air are not dependent on the fineness of the cement. With mixtures containing the normal 20–25% of cement, the strength increases about 1% for an increase of 1% in the cement content and this effect was more marked in mixtures poor in cement. As the strength of concrete varies inversely as the amount of water used, a stronger concrete that works quite as easily can be obtained if a larger amount of cement is employed. D. A. Abrams[61] has also recorded tests, extending over a period of 2 years, of the effect of storage of cement under varying conditions. Compressive tests of the concrete and mortar showed that deterioration occurred chiefly during the first 3 months, and at the end of 2 years amounted to 40%. The duration of storage seems more important than the conditions, provided direct access of moisture is avoided. Storage is said to prolong the time of initial and final setting and only slightly affects the consistency, and the deterioration seems to be due to the absorption of atmospheric moisture. E. H. Lewis[62] has pointed out that whilst most blast-furnace slags can be used for the manufacture of Portland cement, only some are suitable for addition, before grinding, to Portland cement clinker for making the so-called "iron" cement. There is no relation between the suitability of slags for this purpose, or for use as an aggregate, and the suitability for manufacturing cement. The author also advocates that cements made from slags other than blast-furnace slags should be distinguished from cements made from blast-furnace slag, as the former often contain an excess of sulphur and are of poor quality. F. C. Lea[63] has found that the breaking strength of steel used for reinforcing concrete is reduced to 7 tons per sq. in. if heated to about 640° C., so that concrete beams cannot be expected to stand very long if subjected to such a temperature for any length of time. Further, tests made on concrete cylinders and on cement briquettes and cubes indicated that the usual thickness of cement employed does not afford sufficient heat insulation to prevent the steel from attaining that temperature, if the structure is exposed to a fierce fire for several hours. I. Hiroi[64] has published an account of experiments on Portland cement and hydraulic lime that have been going on for 20 years, bearing mainly on the resistance to the action of sea-water. Where sound cement was used, no case of decomposition of the cement by the chemical action of sea-water was found. "Neat" cement briquettes attained their maximum strength in less than a year, and though they rapidly became weaker to tension, they remained intact and even showed increased compressive strength. A series of crushing strengths of mortar briquettes, made with "standard," coarse beach, and fine sand (passed through a sieve of 220 meshes per sq. cm.) showed the superiority of the coarser grades of sand for this purpose. The use of volcanic ashes in mortar is of no advantage in air, but in sea water considerably increased strength was obtained with properly proportioned mixtures of suitable ash, cement, and sand. The experiments also confirmed the beneficial effects of ramming mortar and concrete instead of pouring; the benefit is not due merely to the diminished amount of water required in the case of ramming, for the water content does not appear to have any ultimate effect on the strength. F. Ferrari[65] points out that puzzuolana and similar materials when added to mixtures of Portland cement and sand tend to counteract the excessive basicity of hydrated calcareous cements of the Portland type, and considers that the permeability of set cements to dissolved salts must be ascribed to the basicity. Although mixtures of Portland cement and puzzuolana, which are often rich in calcium aluminates, do not resist the action of sea water, mixtures of these materials with sand can be made in such a way that the lime formed on hydration is fixed by the puzzuolana and sand and these products are practically impermeable to dissolved salts and are stronger than Portland cement.

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[50] *Ibid.*, 1920, **3**, 560; *J.*, 1920, 599A.

[51] *Ibid.*, 1920, **3**, 316; *J.*, 1920, 546A.

[52] *Zement*, 1919, **8**, 319, 334, 347; *J.*, 1920, 25A.

[53] *Philippine J. Sci.*, 1919, **15**, 107; *J.*, 1920, 297A.

[54] *J. Amer. Cer. Soc.*, 1919, **2**, 708; *J.*, 1919, 904A.

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[55] *Zement*, 1920, **9**, 61, 74, 85; *J.*, 1920, 451A.

[56] *Zement*, 1919, **8**, 499, 511, 523, 536, 548; *J.*, 1920, 367A.

[57] *Chem.-Zeit.*, 1920, **44**, 562; *J.*, 1920, 599A.

[58] *Philippine J. Sci.*, 1919, **14**, 221; *J.*, 1920, 336A.

[59] *Zement*, 1920, **9**, 319, 429; *J.*, 1920, 784A.

[60] *Proc. Amer. Soc. Testing Materials*, **19**, Pt. II.; *J.*, 1920, 297A.

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[61] *Structural Materials Research Lab., Lewis Inst., Chicago, Bull.* 6; *J.*, 1920, 547A.

[62] *J. Iron and Steel Inst.*, 1920, **101**, 111; *J.*, 1920, 409A.

[63] *Engineering*, 1920, **110**, 293; *J.*, 1920, 661A.

[64] *J. Coll. Eng., Tokyo Imp. Univ.*, 1920, **10**, 155; *J.*, 1920, 690A.

H. Burchartz[66] has published the final results of a series of tests, extending over a period of five years, on the suitability of blast-furnace slags for making concrete. As no alteration occurred in the slags after storage for five years, nor in the concrete after two years, it is assumed that slags can be relied upon to yield as good results as gravel. In connexion with the stability of slags, K. Endell[67] has examined microscopically thin sections of a number of samples. A number of mineralogical constituents were identified. The stability of slags appears to be more dependent on these and on general physical structure than on chemical composition. The stability of fresh slags may apparently be predicted with a fair degree of certainty from such micropetrographic methods. It is also stated that slags that show no obvious signs of disintegration after the lapse of six weeks may safely be used as aggregate for concrete.

With regard to another material, boiler-clinker, for use as an aggregate for concrete, Nitzsche[68] considers that it should have a volume weight, when loosely filled, of 0·72 and a sp. gr. of 2·15, and points out that it is advisable to control the proportion of sulphates and ferrous oxide in order to avoid unburnt material. D. H. Fuller[69] has recorded the results of experiments on clays, fired for the purpose of yielding a light vesicular mass suitable for concrete aggregate. Rapid firing, under reducing conditions, in a rotary kiln is the process advocated; clays and shales that "over-fire" easily are most useful raw materials. The method of testing was to grind, pug, and mould the material into 2-in. cubes, which were fired to a temperature of 1375° C. in 6 hrs., trial pieces being withdrawn every half-hour. The structure of the specimens is noted and any which fail to float in a salt solution of sp. gr. 1·1 or which have a dense external shell and enclose large cavities are considered unsuitable. D. A. Abrams[70] has carried out tests on the effect of tamping, vibration, and jigging on concrete that has to be forced into intricate moulds, or where reinforcement is used, and finds that these are of value for the purpose, provided they are applied before completion of the moulding, or before the concrete sets, but otherwise they are harmful. Tamping etc. has the effect of reducing the strength of concrete, but has the advantages that the concrete can be placed in position with greater certainty, a coarser aggregate can be used, and consequently less water, so that the mass can be worked drier. The United States Bureau of Standards has issued a Report[71] on bituminous coatings for rendering concrete surfaces acid-proof. The coatings are classified as paints, enamels, or mastics. The paints consist of bitumen or coal-tar pitch, thinned with a solvent; enamels are mixtures of bitumen of high melting-point thoroughly incorporated with finely-divided silicious filler, and mastics are mixtures of hard asphalt, finely powdered silicious filler, and properly graded coarse sand or aggregate. A priming coat of bitumen, thinned, is applied and when it has dried to a tacky condition the mastic is applied hot. Several layers should be spread over the clean surface until a thickness of about 1 inch is obtained.

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[65] *Giorn. Chim. Ind. Appl.*, 1920, **2**, 238; *J.*, 1920, 821A.

[66] *Stahl u. Eisen*, 1920, **40**, 814; *J.*, 1920, 573A.

[67] *Ibid.*, 1920, **40**, 213, 258; *J.*, 1920, 297A.

[68] *Zement*, 1920, **9**, 146, 152, 158, 195; *J.*, 1920, 573A.

[69] *J. Amer. Cer. Soc.*, 1920, **3**, 256; *J.*, 1920, 491A.

V. Kohlschütter and G. Walther[72] have made an experimental study of the hydration of lime in support of their theory of the colloidal state. The slaking of lime up to true solution comprises several stages, resulting in the formation of (1) calcium hydroxide, (2) hydrated forms of the hydroxide, (3) lime cream, a non-settling suspension, (4) milk of lime, a colloidal suspension of lime in the saturated solution, and (5) lime water, a true solution. No very definite conclusions could be drawn from the experiments, but they do confirm the practical experiences that the structure of the material from which the lime is made has a great influence on the slaking power, on the character of the lime cream, and on the hardening properties of the mortar. F. Hartner[73] has experimented with anhydrite for use as mortar and states that if the material is ground to pass a sieve of 5000 meshes per sq. cm., or if 1–3% of lime or Portland cement be added to coarser ground material, anhydrite which ordinarily is too slow, sets in a few hours. Results of tensile strength and resistance tests are given for anhydrite alone and also admixed with lime and Portland cement, and it is claimed that the fuel consumption in the case of anhydrite-mortar is about 6–10%, but for lime it amounts to about 20–30%, for gypsum about 15–30%, and for Portland cement about 40–60%, and also that the losses in manufacture are negligible, which is not the case with lime, gypsum, and Portland cement.

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[70] *Structural Materials Res. Lab., Lewis Inst., Chicago, Bull.* 3; *J.*, 1920, 112A.

[71] *Chem. and Met. Eng.*, 1920, **23**, 287; *J.*, 1920, 664A.

[72] *Z. Elektrochem.*, 1919, **25**, 159; *J.*, 1920, 25A.

[73] *Z. angew. Chem.*, 1920, **33**, 175; *J.*, 1920, 573A.

G. R. Thompson[74] in discussing the old problem of the use of straw by the Israelites in making bricks in Egypt, expresses the opinion that the straw was merely chopped and used to prevent the clay from sticking to the hand of the worker, or to the ground during drying when moulded. The composition of some bricks of undoubted Jewish origin closely resembled that of the Nile mud, and no trace of straw was found in them. R. Malfait[75] states that granulated slag contains usually an excessive amount of water, which can be reduced to about 6–12% by storage under cover for a month, when the slag can be easily ground. The water still remaining effects the hydration of the calcium silicate, which forms the chief binding agent in the bricks, but any surplus water causes disintegration. Although slag bricks are less porous than those made of clay, they should not be used in positions where they will come in contact with sea water. A. Guttmann[76] has given details of the Schol process for making a light-weight artificial stone from blast-furnace slag. This should contain 35–38% SiO_2 and not less than 44–47% CaO. The light spongy material is obtained by projecting the molten mass into a limited amount of water. It is crushed, sifted, and mixed with quicklime and the articles hardened by steam heat.

Kröhnke[77] has discussed the relation of natural rock asphalt to the artificial product obtained by the Zimmer process. The natural stone can be compressed to a hard mass; if heated to 120° C. it crumbles to a brown powder which can be compressed to a mass of even higher density, but loses this property if heated above 150° C. The artificial products are mixtures of bitumen and finely powdered mineral matter. Zimmer considers that the mineral matter in the natural product is chemically combined by means of sulphonated acids present, and it is suggested that the artificial product is superior on account of its higher dropping point and its lower solidifying point. L. F. Hawley and O. Kress[78] have experimented to ascertain if the recovery of pitch from waste roofing felt is practicable on a commercial scale. About 50–60% of pitch was recovered from the material by extraction three times with gasoline, and on a works scale four extractions with 350 gallons of solvent to 1 ton of waste should give about the same result.

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[74] *Analyst*, 1920, **44**, 403; *J.*, 1920, 65A.

[75] *Rev. Mat. Construction et Trav. Publ.*, 1919, **123**, 335; *J.*, 1920, 192A.

[76] *Stahl u. Eisen*, 1920, **40**, 326; *J.*, 1920, 298A.

[77] *Chem.-Zeit.*, 1920, **44**, 253; *J.*, 1920, 336A.

[78] *Paper*, 1920, **27**, 18; *J.*, 1920, 821A.

D. W. Kessler[79] has given a very full account of a number of physical and chemical tests of commercial marbles of the United States which should form a useful addition to our knowledge of the applicability of marble for constructional purposes.

F. Moll[80] has given a short history of the use of inorganic salts for preserving wood and the work of Wolman who introduced the use of salts of organic acids and reduced the temperature of treatment. In present practice, sodium fluoride is largely employed, and when water-soluble organic compounds are also used, these are fixed by some chromium salt. With regard to sodium fluoride, H. Devaux and H. Bouygues[81] point out that although an efficient antiseptic against certain organisms, it is useless for injection into railway sleepers, for example, as these are exposed to water and the salt is rapidly dissolved away by rain. R. Falck[82] prepared pure cultures of wood-destroying fungi and added them to woods impregnated with various preservatives, and found that only strong preservatives, such as sodium fluoride, dinitrophenol, etc., in high concentration, were really effective. Copper hydroxide, a favourite spray for plants, is of no use in preserving wood. He also recommends a 10% "resinol-lime" or "resinol-magnesia" as a spray liquid. E. Bateman[83] has called attention to the fact that the analysis of a wood treated with an inorganic salt as preservative seldom shows the same amount of salt absorbed as that calculated from the increase of weight of the wood after treatment, and concordant results are obtained only when perfectly dry wood is treated. There is no reason to suppose that any chemical combination occurs between the wood and the solution of the usual inorganic salts employed as preservatives.

E. Bateman[84] has also pointed out that a definite relation exists between the absolute viscosity of creosote and its penetration into wood. In addition to viscosity the factors affecting penetration are time of treatment, pressure during application, and variations in the wood, but the effects of changes in these factors are not known.

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[79] *U.S. Bureau of Standards, Tech. Paper* 123 ; *J.*, 1920, 112A.

[80] *Z. angew. Chem.*, 1920, **33**, 39 ; *J.*, 1920, 236A.

[81] *Comptes rend.*, 1920, **170**, 1006 ; *J.*, 1920, 409A.

[82] *Z. angew. Botanik*, 1919, 11 ; *J.*, 1920, 171A.

[83] *Chem. and Met. Eng.*, 1920, **22**, 57 ; *J.*, 1920, 193A.

[84] *Ibid.*, 1920, **22**, 359 ; *J.*, 1920, 336A.

IRON AND STEEL.

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THE year 1920 has been one of anxiety for the majority of iron and steel manufacturers. With the advent of peace, the whole trade has undergone a transformation, for, whereas during the war special steels such as nickel and nickel-chrome steels were in great demand, requests for such material have been reduced to a minimum. The demand for carbon steels, especially for the shipping industry, has been good, in some cases greater than the supply, but there are signs of a falling off in this, due to the cancelling of many contracts and decreased production of shipping vessels.

The supply of foundry pig, from all accounts, is below that required, with the resulting shortage of castings. New furnaces have, however, recently been put under blast in many districts, thereby improving the outlook in this direction.

The third quarter of the year has shown an improvement in both exported and imported material,[1] imports from Belgium having particularly increased, especially in the matter of tool steel, this being on account of the lower price asked, compared with British firms.

Production in all European countries has far from reached pre-war levels, the trade in France being in a particularly unstable condition, whilst that of Italy may be duly pronounced as bad. Germany is suffering from shortage of coal, but notwithstanding this, appears to be employing great efforts to restore the industry to its normal state.

New blast furnaces are to be erected in Holland, this being part of a larger scheme.[2]

The countries in which progress seems to be greatest are those in which the industry has been newly established, British Columbia and Australia paying particular attention to the industry, whilst the possibility of Switzerland becoming an iron smelting country on a small scale does not seem to be far remote.[3]

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[1] *Iron and Coal Trade Rev.*, 1920.

[2] *Ibid.*, October 15, 1920.

[3] *Ibid.*. October 15. 1920.

American competition has not been quite so keen as was expected, although numerous accounts indicate that American prices are lower than British.

The cause for this instability of trade is not far to seek; it lies in the main with the questions of labour and prices. The disinterestedness of manufactures in the technical application of scientific work does not improve matters, the old idea of economy, involving depletion of staff, having replaced the more modern ideas of increased efficiency and the introduction of progressive methods.

IRON ORES.

An interesting account of the utilisation of titahiferous iron ore in New Zealand is given by J. A. Heskett.[4] The ore in question is the Taranaki iron sand containing 57·3% of iron, which exists in the ore in the form of FeO and Fe_2O_3, being essentially of a magnetic nature. The gangue being practically free, magnetic concentration can be resorted to. The method of smelting employed was to powder the ore, along with coal, briquette, carbonise the block, and smelt the mixture in a small blast furnace using a pipe stove. The pig formed contained about 3·59% C, 1·60% S, 0·63% Ti, 0·51% P, and 0·45% Mn. The slags were found to be fluid, and no trouble arose in handling them.

An account of the smelting of these ores is also given by V. W. Aubel.[5]

BLAST FURNACE PRACTICE.

Blast furnace practice has been well supplied with literature this year, no less than five papers having been read before the Iron and Steel Institute within six months. Dealing with the chemical and thermal conditions in blast furnace practice, H. E. Wright[6] points out the insufficiency of the heat evolved by chemical reaction in a blast furnace, to supply the necessary heat for smelting. After considering in some detail the relative possible amounts of carbon monoxide and dioxide under different conditions, the author sums up the combustion of the fuel as follows: (*a*) Chemical reactions render it possible for not exceeding 5·8 cwt. of carbon as carbon monoxide to be further burned to carbon dioxide. (*b*) Chemical reactions involved in the decomposition of carbon dioxide from material, and in the process of direct reduction of metallic oxide or metalloids, form carbon monoxide without air being necessary. (*c*) The combustion of carbon, at the tuyères by air, and by oxygen from the moisture it contains, is, apart from the use of hot blast, the only other means available of making good any heat required after the above reactions have been fully carried out. He also points out the importance of the factor relating to the reducibility of the ore, giving figures of reducibility of 90 in the case of calcined Cleveland ironstone, compared with 19 in the case of magnetite. The influence of the time factor (*i.e.*, time taken for charge to descend), impurities in ore, etc., are also dealt with, and their effect upon the coke consumption considered. The author becomes particularly interesting when he deals with the question of slag, stating that a new theory is required in order to place the slag question on a new footing. One would judge from statements made, that the author was unacquainted with the important work of Rankin and Wright,[7] and of Feild and Royster,[8] the former by working out the complete ternary system lime-alumina-silica, and the latter through their invaluable experiments giving exhaustive data relating to the viscosity of slag over wide ranges of temperature and composition, have erected a monumental guide to blast-furnacemen.

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[4] *J. Iron and Steel Inst.*, 1920, **51**, 201; *J.*, 1920, 451A.

[5] *Bull. Amer. Inst. Min. Eng.*, 1919, 2081.

[6] *J. Iron and Steel Inst.*, 1920, **51**, 179; *J.*, 1920, 410A.

F. Clements[9] wisely advocated the maintaining of a chemical balance in blast-furnace practice. He gives very complete figures relating to the heat and chemical balance of furnaces, and concludes that the total carbon consumed is proportional to the area of the bosh, the rate of making iron being naturally proportional to the same factor. Drawings are given of a furnace and a layout of a unit capable of an average output of 250 tons per day, from a burden giving a pig yield of 30 %. Although Johnson's book on "Principles, Operations, and Products of the Blast Furnace," is referred to in the bibliography at the end of the paper, but little attention seems to have been given to the contents of that book, no comments being made upon the method of calculating thermal efficiency advocated by the latter writer. Johnson, it will be recalled, suggests two thermal equations to represent the true conditions of a blast furnace, one for the hearth and one for the shaft. He also works on the basis of a critical slag temperature, and points out the application of the second law of thermodynamics to blast-furnace reactions, showing that what really matters is not so much the quantity of heat, but rather the intensity.

It is a pity that British blast-furnacemen do not pay more attention to American work and American practice, not so much with a view to copying, but rather for the purpose of selecting what might be readily applied in this country. Every furnaceman should read Johnson's book and the papers by Rankin and Wright, and Feild and Royster cited (*loc. cit.*).

C. H. Ridsdale's paper on the valuation of ores and iron-making material,[10] forms a happy link between the two contributions just dealt with. The author suggests that ores should be purchased at their net value, based upon scientific calculation. Obviously the value of an ore depends upon the amount of iron that can be got from it, and also on the expenditure involved in its extraction. The author deals separately with the various impurities that usually exist in the ore, considering these from the standpoint of their valuation.

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[7] *Amer. J. Sci.*, 1915, **39**, 1.

[8] *U.S. Bur. Mines, Tech. Papers* 187, 189 ; *cf. J.*, 1918, 246A, 548A.

[9] *J. Iron and Steel Inst.*, 1920, **51**, 125 ; *J.*, 1920, 410A.

W. W. Hollings[11] in a short paper on the variations in the heat supplied to the blast furnace, and their effect on the fuel consumption, gives reasons for concluding that it would not pay to dry the blast in countries with low average air moisture, whilst the addition of excess oxygen to the blast is not likely to result in any appreciable saving.

A. McWilliam[12] gives an interesting account of Indian iron making at Mirjati Chota Nagpur.

A. Hutchinson and E. Bury[13] describe the process of rough-cleaning of blast furnace gas at Skinningrove by the Lodge electrostatic process, and to judge from their results the process has every promise of success. With the use of but 80–85% of the electrostatic plant they have already succeeded in reducing the dust in the gas from 5–6 grams per cb. m. to 0·8–1·1 g. The results of their tests seem to show a distinct saving, not only due to the potassium chloride collected, but also due to a lowering of gas consumption and cost of cleaning of stoves etc.

A question closely allied to gas cleaning is removal of flue dust, and re-smelting it. R. W. H. Atcherson[14] deals with the question of blast furnace flue dust at some length. He states that a decrease in flue dust may be effected (1) by properly grading and mixing the ore, (2) by providing ample gas areas in the furnace top and downcomers, thereby lessening the velocity of the current, (3) by using hard grade coke, and high grade fluxing material.

The blowing engines would appear to have a considerable bearing on the matter; for instance with a turbine blower the current of air is less oscillating than is usually the case with a reciprocating type, and it is this variation in delivery, rather than the velocity, that increases the proportion of fume carried up. By allowing the fume to weather, thereby washing out much of the coke dust, it has become possible to re-charge the decarbonised fume into the furnaces again, with success.

A. Torkar[15] describes a patent process for the manufacture of pig iron in which the use of coke, excepting that required for direct carburisation of the iron, is dispensed with, smelting being carried out by gas resulting from the distillation of lignite. The results obtained from this process should be interesting.

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[10] *J. Iron and Steel Inst.*, **51**, 149; *J.*, 1920, 451A.

[11] *Ibid.*, **52**, 91; *J.*, 1920, 691A.

[12] *Ibid.*, **52**, 159.

[13] *Ibid.*, **52**, 65; *J.*, 1920, 751A.

[14] *Bull. Amer. Inst. Min. Eng.*, 1920, No. 158.

[15] *Mitt. Inst. Kohlenvergasung*, 1919, **1**, 85; *J.*, 1920, 268A.

L. P. Ross [16] gives an interesting explanation for the deterioration of the bricks at the furnace throat, when using steel scrap as part of the charge. He found in this case the deterioration to be due to the oxide of iron formed by oxidation of the scrap acting as catalyst, decomposing the carbon monoxide with the result that the carbonaceous deposit thus formed caused a reduction of the iron oxide in the brick with its consequent disintegration. Therefore, he says, bricks free from oxide of iron should be used.

STEEL SMELTING.

P. Jolly[17] describes a process in which a tilting furnace is used. Starting with a cold or molten pig, by using a good tilting furnace, he states that it is possible to obtain at a lower cost, a steel equal in quality to that of a stationary furnace, using hæmatite pig. The process described differs only in small details from those already used. The employment of cold coke-oven gas for heating open-hearth furnaces is dealt with by F. Springorum.[18] He states that for good results with this gas, the calorific power should be 4300 to 4500 Cals.; with such a gas the consumption is about 300 cb. m. per ton of steel. One advantage appears to be that the gas is free from sulphur.

F. A. Matthewman[19] suggests that in order to avoid the steel taking up sulphur during melting in an open-hearth furnace, the scrap be first coated with a covering of clay wash or silica paint. This suggestion, to judge from the discussion, did not meet with universal approval. A. Schneider [20] advocates the use of a mixture of blast-furnace and coke-oven gases for heating open-hearth furnaces, the temperature being regulated by varying the relative amounts of the two gases.

An excellent description of acid open-hearth practice is given by B. E. L. De Mare.[21] He ascribes the superiority of acid steel over basic to freedom from deoxidation products. Fuel oil is advocated, in preference to producer gas, as giving longer life to the furnace. He advises early additions of ore and limestone, and the use of the highest possible temperatures. In the process described, no additions are made after tapping, the fuel and air being shut off an hour before tapping, and the steel further cooled by holding in the ladle for half an hour. There are not many steel makers who would risk holding the metal for that length of time in the ladle, but there is but little doubt that if this could be done better and sounder steel would result.

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[16] *Iron Age*, 1920, **105**, 117.

[17] *Rev. Mét.*, 1920, **17**, 31.

[18] *Stahl u. Eisen*, 1920, **40**, 9 ; *J.*, 1920, 299A.

[19] *J. West Scotland Iron and Steel Inst.*, 1919–1920, **27**, 34.

[20] *Stahl u. Eisen*, 1920, **40**, 501 ; *J.*, 1920, 410A.

[21] *Blast Fur. and Steel Plant*, 1920, **8**, 318, 385.

E. Piwowarski[22] considers from an exceedingly logical standpoint, the use of ferrosilicon as a deoxidiser. When the ferro-alloy is added early on, the gases which would ordinarily escape during cooling, are thereby entrapped, whilst if the steel be first allowed to cool, and then the necessary addition be made, more perfect deoxidation will result. Considering the last two papers together, it would seem desirable, if it were possible, to add the ferrosilicon after the metal has been allowed to remain in the ladle for some time.

H. M. Howe[23] makes some excellent suggestions with regard to the construction of open-hearth furnaces. Heat exchanges in the regenerators call for a dense and even semi-glazed refractory. A hard brick of high thermal conductivity, even if too fusible for the upper part of the chequers, might with advantage be used in the lower cooler parts. In order to increase the surface area, thin bricks might be used, and by ribbing the sides, the tendency for them to catch dust will be lessened. The use of water-cooled ports should be considered carefully with regard to the heat loss involved. Howe comments on the importance of slag composition, and of controlling this, especially with reference to the iron oxide content. The precise maxima of iron oxide allowable for the various processes should be ascertained, whilst the methods of elimination of harmful inclusions should receive careful consideration.

Other questions that arise are, how far is the objection to the use of ore justified; whether in making fine steel, residual manganese should be insisted on; and also what are the relative merits of high and low casting temperature? The relative merits of the acid and basic process, and also of the various duplex and triplex processes need further investigation.

Howe's paper is an exceedingly valuable contribution. Unfortunately steel making processes are but seldom dealt with at length by any author, unless the paper in question is concerned with some patented process. Probably no two steel makers employ exactly the same methods, and yet the majority produce good steel. How much better it would be for the community at large if a conference of steel makers were held, at which each maker would divulge his so-called secrets, thrash out the whole subject, and finally agree upon the essential details of the best methods of working.

The question of casting temperature is a matter of controversy, some believing in a high temperature, and others in a low;

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[22] *Stahl u. Eisen*, 1920, **40**, 773; *J.*, 1920, 574A.

[23] *Iron Age*, 1920, **105**, 545.

undoubtedly both have their good and bad effects, but one must essentially be better than the other when all the pros and cons are considered.

SLAGS.

Metallurgists are at last beginning to realise that the substance that they throw away is worthy of attention, recent years having produced many papers of importance dealing with this question.

In an excellent article on the desulphurisation and dephosphorisation of iron and steel by slags, G. Vié[24] states that below 1300° C. a very large proportion of the phosphorus is oxidised ahead of the carbon, but at higher temperatures the carbon is almost entirely burned when the phosphorus begins to be oxidised. A slag of more than 30% SiO_2, does not permit of the phosphorus content being brought below 0·06%, the silica content of a slag being of greater importance than the phosphorus content; 1% of SiO_2 would seem to have the effect of 1·4% of P_2O_5. With regard to sulphur, manganese, silicon, and carbon diminish the solubility of sulphur in iron, the manganese sulphide being only slightly soluble in iron, but highly soluble in a basic slag. In order to desulphurise in a blast furnace it is necessary to introduce a predetermined amount of manganese, and to provide an abundance of slag with an index of less than one. This practice will naturally necessitate a high temperature, and correspondingly large coke consumption. In steel smelting processes manganese additions made previous to every lime addition, cause the manganese sulphide thus formed to rise to the surface, and there be slagged off. It is emphasised that desulphurisation is more complete with pig than with steel, so that it is better to treat the pig previous to its being refined.

B. Yaneske and G. A. Wood[25] in considering acid open-hearth slags, put forward the theory that reduction of silica from the slag to form silicon in the metal is not due to the reaction $SiO_2+2C=Si+2CO$, but that iron is the effective reducing agent, $SiO_2+2Fe=Si+2\,FeO$. The correctness of this statement is evidenced by the fact that when the carbon in the bath is high, its elimination in no way corresponds with reduction of silica from the hearth; in other words, silica may be reduced to an extent far greater than is allowed for by decrease in carbon in the bath, on the basis of the equation $SiO_2+2C=Si+2CO$. The authors strongly advocate the use of limestone in acid practice, not merely as an addition to be made towards the end of the process, but to be added along with the ore additions. This paper is really a further confirmation of results previously published.[26] J. F. Wilson[27] deals with slag conditions pertaining to the basic process. The first slag formed in the basic process, he states, is highly silicious, and constitutes the slag of lowest critical viscosity temperature. Such slags may be divided into two distinct types, the olivine type, and the mellilite type. Silicates high in phosphorus will nearly all be of the olivine type, the lime taken up by the phosphate reducing that available for combination with the silica. The disadvantage of great slag bulk is discussed : the larger the volume of slag over the metal, the greater will the blanketing effect be ; the smaller the volume and less the viscosity of the slag, the lower will the oxide content of the finished steel be.

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[24] *L'Age de Fer*, 1920, **36**, 189.

[25] *J. Iron and Steel Inst.*, 1920, **51**, 287; *J.*, 1920, 410A.

[26] *Ibid.*, 1919, **49**, 257; *J.*, 1919, 537A.

[27] *Ibid.*, 1920, **51**, 266; *J.*, 1920, 410A.

METALLOGRAPHY AND CRYSTALLOGRAPHY.

G. F. Comstock and W. E. Ruder[28] give a *résumé* of the important literature relating to nitrogen in steel. The addition of titanium is shown to reduce the amount of nitrogen. Typical photomicrographs of titanium nitride are given. This is a hard, angular constituent, orange-pink in medium and high carbon steels, and yellow in low carbon steels. It is shown that nitrogen may occur in eutectoid patches as needles at the grain boundaries, or remain in solid solution. For microscopical examination, annealed steels must be used.

H. S. Rawdon and H. Scott[29] deal with the microstructure of iron and mild steels at high temperatures, studying the effect of changes of the surface layer when heated *in vacuo* to high temperatures. They observed no characteristic crystal form corresponding with the so-called β range.

F. Giolitti[30] apparently still believes in the existence of β-iron, for he says that β-iron assumes a granular, and α-iron a lamellar habit; this accounts for the production of the Widmanstatten structure in low carbon steels. In a further paper[31] the same author discusses the relation between dendritic structure and ferrite mesh.

J. H. Whiteley[32] deals with the distribution of phosphorus in steel between the Ac1 and Ac3 points. During the heating to a temperature between these critical points it is alleged that the phosphorus diffuses from the γ- to the α-iron, the phosphorus being more soluble in the latter form than in the former ; the lowering of the solubility in the γ-form is due to the carbon in solution. Whilst diffusion of phosphorus at temperatures below 650° in ferrite takes place extremely slowly, at temperatures above this it takes place more rapidly, whilst at 800° or above it is quite rapid. The velocity of diffusion in γ-iron likewise increases with temperature, but is never so rapid, whilst at or near the Ac3 point the speed of diffusion suddenly diminishes. Whiteley suggests a method for the removal of ghosts, which is to heat the steel to a temperature just below the Ac3 point; this serves to remove completely the excess of phosphorus in the ghosts areas of the γ-iron. This treatment does not completely remove the ghosts, however, since these are due to substances other than phosphorus.

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[28] *Chem. and Met. Eng.*, 1920, **22**, 399 ; *J.*, 1920, 337A.

[29] *Ibid.*, **22**, 787 ; *J.*, 1920, 452A.

[30] *Ibid.*, **22**, 585 ; *J.*, 1920, 410A.

[31] *Ibid.*, **22**, 757.

[32] *J. Iron and Steel Inst.*, 1920, **51**, 359 ; *J.*, 1920, 452A.

W. E. Hughes[33] describes the microstructure of electrolytic iron, deposited under various conditions.

C. K. Burgess[34] discusses the structure of steel at high temperature, the detection of causes of failure, and the identification of unusual elements in steel. Photomicrographs are given.

Two papers published in American journals deal with the question of deep etching of steel rails. F. M. Waring and K. E. Hofamann[35] show how deep etching develops, or rather shows up defects not observed by micro-examination. H. S. Rawdon[36] uses as etching medium hot hydrochloric acid (sp. gr. 1·9), which brings out the fissures very plainly. Another method of etching, also adopted with success, was to magnetise the specimen, and immerse it in kerosene oil containing fine iron dust in suspension; the particles will then orient themselves to the shape of the discontinuity.

P. Oberhoffer and W. Oertel[37] have studied the relation between mechanical work and grain growth in an electrolytic iron. The recrystallisation temperature depends, they find, upon the amount of strain in the metal, this temperature being lower as the stress is increased. Providing the amount of deformation was slight, the grain growth was rapid even below the critical range.

HEAT TREATMENT AND MECHANICAL TESTING.

The important work of the year with reference to mechanical testing undoubtedly lies in the Report of the Steel Research Committee founded by the Institution of Automobile Engineers and the Society of Motor Manufacturers and Traders,[38] appointed to establish the mechanical properties of the British standard wrought automobile steels.

Certain compositions for steels were first selected; these were then heat-treated by different investigators, generally three or four independent treatments being carried out. From the result of these different tests, the Committee took a mean average of what they considered to represent the true mechanical properties of the steel under consideration.

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[33] *Ibid.*, **51**, 321; *J.*, 1920, 451A.

[34] *L'Age de Fer*, 1920, **36**, 189.

[35] Amer. Soc. Testing Mat., June 25, 1919; *Iron Age*, 1919, **104**, 13.

[36] *Chem. and Met. Eng.*, 1920, **22**, 505.

[37] *Stahl u. Eisen*, 1919, **39**, 1061; *J.*, 1919, 905A.

[38] *Rept. of Steel Research Committee, Inst. Automobile Eng.* (London, price 37/6.)

Complete tensile tests, Izod impact tests, and Charpy and Brinell tests are recorded, and curves showing the relation of these tests to some variable are given. In the introduction to the report, definitions respecting terms used in treatment are given.

The steels dealt with include two carbon case-hardening steels, a 2% nickel and 5% nickel case-hardening steel, a 0·2% and 0·35% plain carbon steel, a 3% nickel steel, 1½% nickel chrome steel, 3% nickel chrome steel, and an air-hardening nickel chrome steel. A high and low limit of analysis was taken for each class cited.

The treatment curves are extremely interesting and will be briefly considered. One set of curves shows the relation between mechanical tests and tempering or reheating temperature on a water-hardened steel containing 0·2% C and 0·99% Mn. The noticeable feature with reference to these curves is the increase in yield brought about between 350° and 450° C., this increase being occasioned by a drop in the maximum stress. A peculiar secondary hardening effect is also apparent between these temperatures. Izod impacts show the greatest variation, increasing rapidly between 300° and 600° C. The figures for elongation show a gradual increase up to 400° C., after which the increase becomes more marked to the higher temperature. An even more interesting set of curves indicates the effect of water-hardening with respect to variation of mass. These tests refer to a case-hardened steel quenched in water at 760° C., after a cementation and refining treatment, the variation in mass being in respect to variation in diameter. The tests, of course, refer to the core. The chief interest in these curves undoubtedly lies in the variation in Izod impact, which gives a figure of about 58·5 ft. lb. with a piece about 0·7 inch diameter, reaches a maximum of nearly 90 ft.-lb. at 1·5 inches, and then rapidly falls to 75 ft.-lb. at 2·1 inches diameter. This clearly indicates that the highest impact figure is attained when the steel is retained in a certain condition, this condition varying between the state of semi-decomposed martensite and lamellar pearlite. Similar results were obtained with a steel containing 0·12% carbon.

Water-hardening followed by tempering at different temperatures, does not produce in steels with low carbon content, *i.e.*, 0·15%, such a marked discontinuity in the Izod curve, this test showing a more gradual increase in value from 100° C. upwards, whilst the yield and maximum stress follow one another.

Hardening and tempering curves of a steel containing 6·0% Ni and 0·17% C are of a more wavy and undetermined nature; the Izod impact shows two breaks, one at about 275° C., where a sudden increase begins, and a decided maximum at 650° C. This point of inflexion at 650° C. appears to be shared more or less by all the mechanical properties.

The idiosyncrasies mentioned appear in many of the curves given; in all cases the Izod test presented the greatest difference, whilst generally speaking oil-hardening produces a more uniform tempering curve than a water-hardening tempering treatment. This is, of course, to be expected.

All the tensile properties vary fairly gradually with size, excepting the Izod test, which falls rapidly when the diameter of piece increases from about 0·7 inch to 1·25 inches.

The pure nickel steels and low chrome-nickel steels present but slight differences from the plain carbon steels, with regard to the contour of the curves. It is when we come to the high chrome-nickel that perhaps the greatest interest accrues. Tests of oil-hardened and tempered steels containing 0·38% C, 1·72% Ni, and 1·65% Cr, relative to different tempering temperatures, indicate normal tensile properties, but the Izod curve again shows an enormous break with respect to a slight difference in temperature. At 600° C. the impact value is about 7 ft.-lb., whilst at a temperature only 50° C. higher its value is nearly 40 ft.-lb. The curves illustrating the variation of properties with increasing diameter give remarkably uniform results, indicating the extreme slowness of reactions in a nickel-chrome steel compared with plain carbon. A steel with 0·20% C, 1·52% Ni, and 0·80% Cr produced a much higher impact value than the previous one, over 90 ft.-lb. at the maximum. This appears to indicate that there is a particular relation between the nickel and chromium content that will produce the best results. The sample containing 0·31% C, 3·27% Ni, and 0·82% Cr is of the highest interest. The treatment given to this steel was to oil-harden at 820° C. before tempering. On tempering, the maximum stress decreases rapidly to 650° C., and rises again to 700° C. The Brinell hardness follows the same course, whilst the elongation is more or less the inverse. The yield point remains constant up to 325° C. and then falls up to 700° C. The reduction of area rises in a rather irregular manner to 650° C. and then decreases. The Izod impact test again presents the greatest peculiarities; the figure for this rises from 11 ft.-lb. at 0° C. to 20 ft.-lb. at 200° C., then falls rapidly to a minimum of about 4 ft.-lb. at 300° C., and from that point rises rapidly to 650° C., where it reaches its maximum value of about 74 ft.-lb., decreasing again at higher temperatures. The effect of diameter on this steel is almost negligible. With a lower chromium content, namely 0·45%, and relatively the same nickel content, *i.e.*, 2·95%, and low carbon, 0·17%, these peculiarities all vanish, the curves conforming to those of a simple carbon or nickel steel.

At the end of the report, thermal curves of all the steels worked with are given. Unfortunately, these are plotted on rather a small scale, and no temperatures below 400° C. appear to have been regarded. The report is undoubtedly full of information, and represents the best practice of steel manufacture. No explanation of the phenomenal variations of tensile and impact properties with varying treatment has been attempted, the investigators giving merely the effects, without venturing upon the cause. This is a pity, for whilst a knowledge of facts is undoubtedly of great importance, and generally speaking sufficient for the engineering community, it can but touch upon the fringe of the question. It is only by knowing the cause that we are fully able to alter, or allow for, the idiosyncrasies of treatment.

W. H. Hatfield[39] gives an excellent account of the mechanical properties of automobile steels; not only does he give the results of a considerable number of tests, and deal with certain steels which are missing from the previous report, but is courageous enough to comment upon the advisability of different steels for different purposes, stipulating the particular steel to be used for the particular parts in automobile construction. As with all other papers by the same author, the discussion is lengthy, and brings out many points of interest. He brings into prominence two of the lesser known methods of testing, viz., the Stanton alternating and the Sankey bend tests. These two test methods came under a vigorous discussion at a paper by W. H. Hatfield and H. M. Duncan,[40] where the question was discussed to its full. The impression given by the critics of these methods is that if they simply confirm figures already derived from tensile tests, why include them in our testing methods? If, however, the results are a criterion of a property fundamentally different from any given by our existing tests, what is the interpretation of this property? The Sankey and Stanton tests, to judge from figures given, vary enormously amongst themselves, and in many cases show no agreement whatever with the figures given by other methods. This alone should in no way curtail research on those lines; what is required is a reason for these variations. Thus one figure obtained from the Sankey test is total energy absorbed. Now a water-quenched tool steel would give a figure for this test of almost zero value, whilst a wrought iron would give probably the highest value. A quenched steel, it should be noted, contains a vast amount of energy locked up, due to quenching, whilst a wrought iron in the dead annealed state contains, practically speaking, no latent energy. The question arises then, is there any relation between the latent energy existent in the material and that absorbed by bending, or in other words, if we give to all material a total energy content, does the difference between this total and the Sankey figure give us the amount of latent energy in the metal? In order to test this, material of great uniformity and homogeneity would be necessary, but it does appear to be an investigation worth carrying out.

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[39] *Automobile Eng.*, 1920, **10**, 243

[40] *Trans. N. E. Coast Inst. Eng.*, 1920, **36**, 321.

Hatfield's antipathy to the Izod test has met with general disapproval; the Izod test does give indication of a property not shown up by any other method—call it notch bar brittleness, or what you will—and in the mind of the writer, it is the test above all. All Hatfield's papers are well worth perusal; they are written by a man with the courage of his convictions, and even if one does not always see eye to eye with the author, one is bound to admit that on the subject of mechanical testing he speaks as an authority.

Impact brittleness has this year again received its quota of papers. A very excellent contribution has been published by R. H. Greaves and J. J. A. Jones.[41] These investigators have carried out an immense amount of work, and given figures showing the effect of different heat treatments upon the Izod impact figure. The authors in their conclusions, admit that up to now no definite explanation has been found for impact brittleness. It is tentatively suggested, however, that brittleness may possibly be connected with "oxide content" of a steel, being due in some way to the presence of chromium oxide. If this view is correct, it must, as the authors apparently suggest, necessitate a reversible solution reaction at about 520° C., that is to say, one must assume that above the critical brittleness temperature the oxide is soluble, whilst below it is insoluble. Reading between the lines it would appear that the authors themselves are not quite satisfied with this explanation.

J. H. Andrew[42] in a paper on casting and heat treatment of steel, gives some interesting figures showing the relation between the phosphorus content and the Izod value. It may be deduced from these results that a steel absolutely free from phosphorus would not be subject to this peculiar form of brittleness. The author's results were confirmed by Dr. Stead, but others were inclined to be sceptical. It cannot be expected that deductions of this character will be readily accepted by steel makers, when there are such things as specifications to be conformed with.

The year 1920 must, then, pass out without a satisfactory solution of the problem of impact brittleness; it will be a surprise, however, if the matter is not completely and conclusively solved in 1921.

J. Descolas,[43] in a paper on the heterotropy of forged steel, discusses the various effects of forging, indicating the relation between the tensile tests and direction of forging. He makes the following recommendations:—(1) For plain relatively long bars, simply roll; (2) for a piece of large diameter and small height, hammer hot; (3) for a piece of large diameter and height, hammer after forging, and work on a mandrel. A test piece taken from material forged equally in three directions, gave equal tests taken in these directions. This latter point is of importance, since it shows that mechanical work rather than the direction of the dendrites influences the test piece.

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[41] *J. Iron and Steel Inst.*, 1920, **52**, 171; *J.*, 1920, 692A.

[42] *Trans. N.E. Coast Inst. Eng.*, 1920, **36**, 355.

[43] *Rev. Mét.*, 1920, **17**, 16.

A contribution to the study of heat treatment of high chrome steels by H. J. French and Y. Yamauchi[44] deals with samples of steels of this type treated in diverse ways. Oil-hardened pieces showed that the Brinell figure increased with hardening temperature up to about 1066° C., above which a decrease is noted, this being due to the retention of some γ-iron. Quenching from about 955° C. is said to develop the best combination of ductility and strength. It is pointed out that ductility is increased by tempering at about 427° C., this increase being less in samples quenched from above 955° C. than in those quenched from below that temperature. This latter point is of interest in so much that it suggests to the present writer that a secondary hardening effect may take place. In dealing with temperature ranges in hardening steel, C. T. Hewitt[45] states that his experiments show that a steel of not less than $\frac{5}{16}$ inch cross-section may be hardened as high as 100° F. above the Ac point without danger of enlarging the grain sufficiently to weaken the steel, providing a long heating is avoided. A. H. Miller,[46] in a paper on some commercial treatments for alloy steels for structural purposes, rightly states that too little attention is paid to the time factor in heat treatment; three variables must be controlled, viz., temperature, time, and rate of cooling. A steel containing 0·35–0·4% C, 3·0% Ni, and 1·5% Cr was chosen for the experiments, a forged piece being heated at a proper annealing temperature for periods varying from just taking up to heat and furnace cooling, to a soaking for 10 hours, followed by furnace cooling. In the original forged piece the ferrite cell lines were not dissolved, and this did not occur until the piece had been held at heat for a period of ½ hour. Slight growth took place in the grain size between this time and the 10-hour limit. It is stated that tempering of this steel following upon quenching should take place as soon after the quenching operation as possible, in order to avoid cracking of the material. The importance of fibre is dealt with.

SPECIAL STEELS AND PHYSICAL PROPERTIES.

Great attention has been paid in recent years to special steels. This is due primarily to war conditions demanding a steel superior in mechanical properties to plain carbon steels, and special steels introduced in this way may be said to have become firmly established.

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[44] *Chem. and Met. Eng.*, 1920, **23**, 13; *J.*, 1920, 600A.

[45] *Iron Age*, 1920, **106**, 639.

[46] *Chem. and Met. Eng.*, 1920, **23**, 113.

Particular attention has been paid to chromium and nickel chromium steels. C. A. Edwards, in two long papers, deals with a very complete series of chrome steels with varying chrome and varying carbon content. The first paper[47] is a continuance of Edwards' work on the effect of cooling velocity upon the temperature of the critical changes. The results may be summarised as follows:—The temperature at which carbides separate from solution, *i.e.*, the temperature of the Ar change, is raised with increasing chromium content, the highest temperature of this change point coinciding with a chromium : carbon ratio of 10 : 1. Annealed steels up to a certain carbon and chromium content contain carbides corresponding with the compound Fe_3C, Cr_3C_2, previously isolated by Arnold. The authors conclude that no such carbide as Cr_4C exists, but favour the existence of a carbide having the formula Cr_5C_2. The influence of high initial temperature is such as to divide the alloys into two different categories. Firstly, those containing more carbon than the ratio of 1 : 10; these possess similar properties to carbon steels. Secondly, those containing a greater chromium content than this ratio, which have much slower critical velocities, *i.e.*, may be cooled at a much slower rate, and still retain their hardness. This subdivision they consider to be accounted for by the two carbides cited, the normal steels, *i.e.*, those behaving like carbon steels, containing the double carbide, Fe_3C,Cr_3C_2, and secondly, the self-hardening steels, containing chromium carbide, Cr_5C_2.

Their final conclusion is strange; it is this: "Whether the increased facility of hardening which is brought about by heating alloys of the second group to high temperatures, is due to the decomposition of Cr_5C_2 into Cr_3C_2 and chromium, or merely to the presence of an excess of chromium retarding the precipitation of carbide from solution, it is at present impossible to say." It is difficult to reconcile the facts. In the first place why does chromium carbide, which ordinarily combines with iron carbide, by existing in a free state, effect self-hardness; it is still more difficult to understand how Cr_5C_2 is formed in annealed steels when it is non-existent at the higher temperatures.

One noteworthy fact about this paper is that whereas hardness determinations are recorded, no curve is given showing any relationship between this property and varying chromium or carbon content. The paper by Edwards and Norbury[48] is restricted to purely electrical resistance measurements, the results from these being considered by the authors to prove their contentions of the first paper.

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[47] C. A. Edwards, H. A. Sutton, and G. Oishi, *J. Iron and Steel Inst.*, 1920 **51**, 403; *J.*, 1920, 453A.

[48] Edwards and A. L. Norbury, *ibid.*, 447; *J.*, 1920, 453A.

The interesting point brought out on considering the two papers together, is that whereas substantial evidence in favour of the compound, Cr_5C_2, is alleged in the first paper, electrical resistivity measurements in the second show no indication of this carbide.

J. H. G. Monypenny,[49] in a paper on the structure of some chromium steels, gives results which in many respects differ from those of Edwards. Monypenny states that there do not appear to be any boundaries which mark out ranges of compositions where the properties change suddenly. He also points out the slowness of solution of carbide in a chrome steel at a temperature above the critical point. The pearlite carbon, he says, does not go into solution abruptly at the critical point but progressively dissolves as the temperature is raised. The suggestion is made that the increased hardness which takes place with increase in initial temperature is probably due to a dissociation taking place in the carbide. The rate of solution of the carbide being less than in carbide steels, a longer time is required for equilibrium. A curve is given showing the effect of chromium upon the eutectoid point, increased chromium giving rise to a eutectoid composition with a decreasing carbon content.

J.H. Andrew, J. E. Rippon, C. P. Miller, and A. Wragg [50] consider a particular set of compositions, the iron-carbon binary, iron-carbon-nickel ternary, and iron-carbon-chromium ternary systems, with all elements excepting carbon constant, being worked out from a physical chemical standpoint, this being followed by the quaternary system iron-carbon-nickel-chromium. The authors give a fairly complete set of determinations of such properties as dilatation, variation of electrical resistivity with temperature, variation in magnetic properties with temperature, and thermal curves. Changes undergone on tempering after hardening are exhaustively dealt with, whilst an explanation of secondary hardening is given. The authors' conclusions are based upon a dissociation hypothesis, which they advance to explain the hardening produced by elevated temperatures in nickel-chrome steels of certain compositions. This suggested explanation is to the effect that at a high temperature, any complex carbides dissociate into iron carbide and the special element, the iron carbide in turn itself dissociating into simpler molecules. This increase in the molecular concentration resulting from the dissociation thereby caused a lowering of the critical point below the normal temperature.

Martensite was shown to be a decomposition product of austenite. It is suggested that this constituent is iron carbide in a state of dissociation, in solution in α-iron. The tempering experiments brought out many points of interest. Objection to the dissociation hypothesis is taken by McCance on the grounds that determinations of the latent heat of transformation of γ- into α-iron give a value for steels which precludes the possibility of carbide existing in anything but simple molecules even at the temperature of transformation. This is a valid and decided objection to the theory, but the authors are not prepared to withdraw it until further evidence has been obtained. Viewing the depression of the transformation point from the molecular standpoint, it appears very necessary to assume a lower molecular weight and increased molecular concentration, to supply a reason for the depression. Definite and accurate values for the specific heat of iron at different temperatures moreover are wanting, so that until these are forthcoming this matter cannot be decided.

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[49] *J. Iron and Steel Inst.*, **51**, 493 ; *J.*, 1920, 453A.

[50] *Ibid.*, **51**, 527 ; *J.*, 1920, 452A.

K. Honda and T. Murakami,[51] in a note on the structural constitution, hardening, and tempering of high-speed steel containing chromium and tungsten, consider in some detail a steel containing about 5% Cr, 18% W, and 0·6% C. In the annealed state according to these authors, the constitution consists of iron dissolving tungsten, free tungstide, and the carbides Cr_4C and WC in a free state. On heating above the Ac point, the following changes take place, $2Cr_4C=Cr_3C_2+5Cr$, and $2WC+3Cr+4Fe=2Fe_2W+Cr_3C_2$. The higher the temperature the more these changes proceed from left to right. During normal cooling from high temperatures the reverse changes proceed but slowly, so that the steel at the ordinary temperature is constituted of these compounds in solid solution. The tempering of high-speed steels is alleged to take place in two steps, at about 400° C. (where the minimum hardness is shown on a secondary hardness-temperature curve), and above 700°.

The self-hardening and resistance to tempering primarily depend upon the quantity of dissolved Cr_3C_2 in iron containing chromium and tungstide, and hence increase with increase in the contents of chromium and carbon respectively. These properties also increase with the maximum temperature, or rate of cooling.

It will be noted that Honda and Murakami believe in the existence of the carbide Cr_4C, a view which is negatived by Edwards with respect to pure chromium-carbon steels.

A paper on the magnetic property of nickel alloys by T. D. Yensen[52] deals with a series of alloys containing between 0 and 100% Ni. In order to make the alloys forgeable, it was found necessary to add a small percentage of either manganese or titanium. The saturation value slowly increases up to 20% Ni, then rapidly to 30%, and again rapidly to 50%, and falls gradually off to 100% Ni. At no point does it exceed the value of pure iron. Reversible and irreversible transformation points studied confirm the results of other workers, excepting that the change from the one form to the other occurs at 34–35% Ni instead of at 30%. The existence of the compound FeNi is considered doubtful; the results rather suggest the existence of a compound Fe_2Ni. From the results obtained an argument is put forward that magnetic and electrical transformations are either atomic or ionic in nature.

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[51] *Ibid.*, **51**, 647 ; *J.*, 1920, 453A.

[52] *J. Inst. Elect. Eng.*, 1920, **39**, 396 ; *cf. J.*, 1920, 411A.

CAST IRON.

H. Scott[53] gives an account of thermal experiments carried out with a steel containing 1·75% C, 0·26% Mn, 2·90% Co, 15·0% Cr; he establishes a relation between maximum temperature and rate of cooling, showing that increase in cooling rate has an effect similar to increase in T max. The results appear to agree with those of the French scientists, and of Andrew, Rippon, Miller, and Wragg, and to conflict with those of Edwards.

The same author[54] gives the results of experiments carried out with five commercial nickel steels, containing from 0 to 3·5% Ni and 0·3 to 0·4% C.

W. Lineham[55] has investigated the hardening of screw gauges with the object of proving that quenching during the passing through a critical point produces the minimum distortion. This was considered to be proved by his experiments, a maximum temperature variation of 10° C. being allowed. Hardening in oil instead of in water produces even less distortion, but in this case a temperature of 717° C., in distinction to 700° C. with water, gives better results.

As regards growth of grey cast iron, M. Okochi and N. Sato[56] derive the interesting information that permanent growth is never produced at temperatures lower than the transformation point, excepting during the first heating; the dilatation curves on heating and cooling to below this transformation coincide with one another, the rapid expansion between 650° C. and the critical point on first heating being due to precipitation of free graphite from the decomposition of Fe_3C. There are two cases of growth, one at the temperature of transformation, and the other above this temperature; both are due to expansion caused by the pressure of the occluded gases. To prevent growth the surface is oxidised, thereby closing the passage against the penetration of gases along the flakes of graphite. It cannot be considered that this paper disposes of the question; many points pertaining to growth of cast iron are still requiring elucidation. What is required is more systematic work, of a nature similar to the work of Carpenter and Rugan, but instead of making all determinations in the cold, it would be better, in the opinion of the writer, to determine the variation of more than one physical property with temperature, making the measurements at the actual temperatures instead of merely determining the effects of temperature by measurements in the cold.

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[53] *U.S. Bur. Standards, Sci. Paper* 335, 1919.

[54] *Ibid., Sci. Paper* 376.

[55] *Engineering,* 1920, **109**, 593.

[56] *J. Coll. Eng., Tokyo Imp. Univ.,* 1920, **10**, 53; *J.,* 1920, 547A.

Cast iron has not received the attention it merits, and a great deal more work is required. If the contention of K. Honda and T. Murakami[57] is correct—and there is no reason to doubt it—namely, that graphitisation is due entirely to occluded carbon monoxide and dioxide, and that an iron is rendered grey or white, according to the amount of these gases that it contains during the passage from the molten to the solid state, it means really that all previous work on cast iron, with respect to the effect of various elements on graphitisation, is more or less useless, and that we shall have to begin all over again. When it is considered that pig as cast from the blast furnace may be of the same elementary composition and yet sometimes come out white and at other times grey, it makes Honda's explanation all the more acceptable. It is indeed an important piece of work, and should place the technique of cast iron manufacture on a sounder basis.

A curious case of a cast iron roll which showed hard white spots during machining is brought to light by B. Osann.[58] The explanation advanced is that during solidification, the contraction due to shrinkage of the solid outer wall forces a part of the molten metal into the riser. The molten part is rich in carbon, and solidifies as grey iron. The part left behind is poorer in carbon, and becomes white, producing a hard spot; the walls of the crystals are therefore harder than the centres, and show as white lines in the fracture. The present writer has himself seen cases of hard and soft spots which occurred indiscriminately distributed throughout the whole casting. It is indeed a source of trouble not only in iron foundries, but sometimes in steel foundries. The explanation given does not therefore appear to solve the matter.

R. S. Archer[59] has shown by a series of chemical analyses and photographs, that graphitisation in white iron can be initiated and completed below the Ar1 point, and cannot be completed above that temperature unless the temperature be very near to it. He states that present evidence is not sufficient to determine whether the saturated solution about to precipitate graphite differs appreciably from that about to precipitate cementite.

CONCLUSIONS.

If one were asked to state the greatest metallurgical event of the year one would answer, without hesitation, "the appointment of

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[57] *J. Iron and Steel Inst.*, 1920, **52**, 287 ; *J.*, 1921, 12A.

[58] *Stahl u. Eisen*, 1920, **40**, 145.

[59] *Bull. Amer. Inst. Min. and Met. Eng.*, 1920, No. 158.

Dr. Stead to the Presidency of the Iron and Steel Institute." Dr. Stead's presidential address[60] is a masterpiece in itself; it is a vivid description of the advances made in the science of metallurgy during the last fifty years.

Signs are not wanting that metallurgy is quickly changing from an art to a science. So far, however, we have trod but little on the scientific pathway; one has not far to go to see methods of works practice which are crude in the extreme, reminding one of ancient times. It is beginning to be realised, however, that metallurgy is nothing more nor less than a branch of physical chemistry, and each year sees more application of advanced physical methods to metallurgical problems. Fifteen or twenty years ago no one would have thought that such properties as dilatation and electrical resistivity would have much bearing upon practical metallurgical problems. One has, however, only to peruse the *Journal of the Iron and Steel Institute* to see that one half the contributions are no less than investigations in physical chemistry.

With the advancement of science, effect is becoming almost of less importance than cause. No man is now content to say that certain changes do take place; he wants to know how, and why.

Many important questions remain unsolved. Impact brittleness, for instance, still requires a solution, and along with it the variations of impact value with treatment. We cannot say that the iron-carbon diagram has reached its final goal; much work is still required on this. The property of so-called self-hardening, along with the effect of initial temperature upon certain special steels, is likewise awaiting solution.

Finality can never be reached, but we can approach nearer and nearer to that state. When it becomes possible to work out all the properties of any combination of metals and non-metals, from tables of their physical constants, we shall have achieved something worthy of the race, but until then investigation must proceed.

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[60] *J. Iron and Steel Inst.*, 1920, **51**, 33.

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METALLURGY OF THE NON-FERROUS METALS.

BY CECIL H. DESCH, D.SC., PH.D.,

Professor of Metallurgy, University of Sheffield.

THE field of non-ferrous metallurgy is a remarkably extensive one, including as it does the extraction from their ores of about 20 metals of industrial importance and a large number of minor interest, the physical and mechanical treatment of the metallic products, the preparation of alloys, and the study of the properties of metals and alloys in relation to their chemical characteristics and constitution. From such a wide field it is only possible to select, for the purposes of a report, a limited number of subjects. The unsettled industrial situation has affected the non-ferrous industries along with others, and it is more than probable that greater technical progress would have had to be recorded had the outlook been less uncertain. On the other hand, the difficulties of international trade and the high costs of transport have led to increased attempts on the part of several countries to become more completely self-supporting in the matter of metal supplies. This scarcely applies to the United Kingdom, except in the small, but interesting case of tungsten, alluded to below. The home production of non-ferrous ores is small. In this connexion reference may be made to the numerous monographs on ore supplies which are now available. The Imperial Mineral Resources Bureau issues pamphlets devoted to individual minerals of economic importance, similar in character to the chapters of the American "Mineral Industry." The Imperial Institute also issues excellent monographs covering much the same ground, whilst the facts relating to home ores and minerals are also contained in the bulletins published by the Geological Survey, the latter being exceptionally full of detail, but suffering from lack of arrangement and orderly presentation. It is unfortunate that these three series, all valuable in themselves, overlap so largely, and some plan of co-ordination and co-operation would seem to be desirable. The Departmental Committee on Non-Ferrous Mining has now issued its report,[1] from which it appears that copper mining is practically extinct in this country, and is not likely to revive. The proposal to subsidise the mining of lead and zinc ores in North Wales is unfavourably criticised by H. Louis,[2] on the grounds that public money has already been spent unprofitably on this scheme, and that any further development is unlikely to bring commensurate benefit to the nation. The plans for increasing the home production of zinc have also proved disappointing, and large plants are standing idle. The annual report of the Department of Scientific and Industrial Research[3] contains several matters of interest. The Standing Committee on Metallurgy has been dissolved, the policy of co-ordinating research by means of such committees having been abandoned since the establishment of industrial research associations. The Tin and Tungsten Research Board has suspended its labours, although it is understood that experiments on flotation and on certain chemical methods of extraction are under examination by firms concerned. The Non-Ferrous Metals Research Association is now in working order, and the work of the Department on copper, zinc, and brass has been transferred to the Association. Excellent work continues to be performed by the Corrosion Committee of the Institute of Metals, this Committee comprising in its membership representatives of manufacturers and users as well as scientific metallurgists. At the request of the Air Ministry, the Research Department set up a committee for the investigation of the corrosion of aluminium and its alloys, but after two meetings had been held it was decided to transfer the work to the Corrosion Committee, this plan having the great advantage that the entire subject of corrosion, so far as the non-ferrous metals are concerned, is now dealt with by a single body, the laboratories and staff being under the supervision of Dr. Bengough, investigator to the Committee. As long experience in this class of work is almost essential to success in the study of corrosion, this arrangement is to be commended.

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[1] *Cmd.* 652.

In France, efforts are being made to render the country far more nearly self-supporting than before. Two copper refineries have been established, together capable of producing 25,000 tons annually, and a large plant for the electrolytic extraction of zinc from mixed lead-zinc ores has been set up in the Pyrenees. It is also intended to carry out the manufacture of nickel in New Caledonia.

The production of aluminium continues to increase. This being one of the metals which Germany was able to obtain during the war, its production has been undertaken in that country, although a supply of sufficiently high-grade ore is lacking, and brown coal has to be used as a source of power, so that it is doubtful whether the industry can survive under competitive conditions. The German substitution of aluminium and zinc for copper and other metals which were unobtainable during the war is mentioned below. Light aluminium alloys are undoubtedly coming to occupy a very important position, but it does not appear that the alloys rich in zinc have such qualities as will cause them to be retained when better metals are available.

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[2] *J.*, 1920, 194R.

[3] *Cmd.* 905.

There has been much activity during the year in the study of alloys, and metallographic methods, which have rendered such admirable service in the steel industry, are making their way rapidly into the non-ferrous industries, although there is a certain conservatism which is not yet completely overcome. The *Journal of the Institute of Metals*, which with its abstracts forms the most complete record of scientific progress in this department of metallurgy, has contained papers of great importance, both for theory and for practice. The *Internationale Zeitschrift für Metallographie*, which has been published in Berlin since 1911, and has been the means of making public many interesting investigations, has now abandoned its international character, and has become a German periodical, under the name of the *Zeitschrift für Metallkunde*, whilst retaining its other principal features, under the editorship of its original director, Dr. Guertler. The largest output of scientific work on the non-ferrous metals is contributed by England and Germany, but important contributions are made from time to time by France, Italy, the United States, and Japan. As in other branches of science having an immediate industrial bearing, however, there is a large mass of published matter of very little real value, and the literature of the subject demands careful sifting.

TREATMENT OF ORES.

The most interesting method of concentration continues to be that of flotation, which has now assumed enormous importance in the treatment of a great variety of ores. The patents have involved much litigation, and this has led to a somewhat acrimonious controversy, even in regard to the scientific principles underlying the process. Reference should be made, however, to several papers dealing with the principles of flotation. That of H. L. Sulman[4] is very important, as coming from one who has been so closely associated with the technical development of the method. The subject is dealt with in relation to surface energy, and the action of frothing reagents is clearly explained. A most interesting discussion of the molecular theory of flotation is contributed by I. Langmuir,[5] who considers the nature of the stable films, one molecule thick, which coat the particles, and explains the relation between the chemical constitution of the oil or other substance used for the flotation, and that of the solid substance to which it adheres. It is probable that in this way light may be thrown on the question, which is still far from having been solved, as to why one mineral floats and another does not. A useful paper bearing on this question is one on the applications of wetting power, by W. H. Nuttall.[6] The separation of molybdenite from quartz diorite and pyrites is described by C. E. Oliver,[7] who states that the ore is ground in a ball mill with a mixture of pine oil and kerosene, the final concentrate containing 85–95% of molybdenite and 2–3% of pyrites. The addition of various organic substances to oil has been tried, and it is stated by E. H. Robie[8] that a mixture of 60% of crude *a*-naphthylamine and 40% of xylidine greatly improves the yield in the concentration of certain copper ores, the proportion of moisture in the filter cake being also diminished. Experimental flotation plant is included in the equipment of the Metallurgical Research Department of the Utah State School of Mines, described by L. W. Chapman.[9] This experimental station deals with ore-dressing and testing in quantities of a ton or more, and also with roasting and with the chloride volatilisation process, which is chiefly applicable to low-grade oxidised ores. Where this process is applied, it is necessary to employ an electrostatic method for the precipitation of fume. Electrostatic precipitation now plays an important part in many non-ferrous smelting operations, since it at once effects a saving of valuable products, and removes a serious nuisance. An account of the electrostatic recovery of arsenic from smelter fumes in Japan is given by R. Hirota and K. Shiga.[10]

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[4] *Trans. Inst. Min. Met.*, 1919-20; *J.*, 1920, 27A.

[5] *Trans. Faraday Soc.*, 1920, **15**, 62.

The usefulness of metallographic methods in the control of smelting operations is shown by an account, by C. G. Maier and G. D. Van Arsdale,[11] of the structure of copper smelter slags. The results show that the copper in the slags is partly in the form of suspended globules of sulphide, whilst the other part, although still in combination with sulphur, is in solution. The globules differ from the original matte in having lost their iron by a reaction with the slag. The quantity of suspended globules, which represents loss of copper, is in direct relation to the quantity of ferric iron present. The investigation is an important one.

The metallurgy of zinc presents several features of interest, although no remarkable developments have occurred during the past year. The general situation in regard to zinc is reviewed by

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[6] *J.*, 1920, 67T.

[7] *Eng. and Min. J.*, 1920, **109**, 840; *J.*, 1920, 412A.

[8] *Eng. and Min. J.*, 1919, **108**, 730; *J.*, 1920, 159A.

[9] *Chem. and Met. Eng.*, 1920, **22**, 877.

[10] *Chem. and Met. Eng.*, 1920, **22**, 276.

[11] *Chem. and Met. Eng.*, 1920, **22**, 1101, 1157.

H. M. Ridge.[12] The European production still lags far behind that which was obtained before the war, and we are mainly dependent on the United States. The outlook for the industry in this country is not regarded as promising, unless the existing works can be modernised and their capacity increased. The electrolytic plants which were operating in England, and produced zinc of high quality, have been closed down, although the United States, Canada, and Tasmania have adopted this process for large new works, situated in each case in favourable positions for obtaining cheap power. The design and construction of distilling furnaces have been so far improved that whilst the reduction of a ton of ore formerly required from 1·4 to 1·5 tons of coal, a recently constructed plant, fitted with counter-current recuperators, shows a consumption of only 0·8 ton. Mechanical furnaces for roasting, and mechanical retort making and charging, have done much to save labour and increase efficiency. The advantages of electrolytic methods for the extraction of zinc, even where water power is not obtainable, are urged by S. Field.[13] Steps are being taken for the production of large quantities of zinc concentrates, and a plant being erected at Kimberley, British Columbia, which is to give an output of 20,000 tons daily, will be the largest in America.[14] The roasting of fine concentrates is described by C. H. Fulton and J. B. Read.[15] The ore is heated to 60°–100° C. and fed into a pipe, where it meets preheated air under pressure, and then passes into a vertical combustion chamber, passing through air heated to 800°. The escaping gases are treated by electrostatic precipitation, and then pass on to a sulphuric acid plant.

Several papers by O. Mühlhäuser deal with the retort process. Some experiments on the influence of pressure on the yield of metallic zinc[16] show that the permeability of different muffles or retorts varies very greatly, and is to be attributed mainly to cracks. When the walls of the muffle are insufficiently gas-tight, the loss of zinc increases with the pressure in the muffle, which should therefore be kept low. The external pressure in the furnace is preferably kept as high as possible. Measurements of the temperature in different parts of a zinc furnace are also given.[17] In a furnace which showed an even distribution of heat throughout its section, those portions in which the retorts were charged with blue powder and other by-products rich in zinc proved to be at a lower temperature than the portions where the charge consisted only of roasted ore, the difference being due to the rapid distillation of zinc from the former at the outset of the heating. The highest temperatures recorded around the retorts were over 1300° C. The variations of temperature during the clearing of the producer and the emptying and charging of the retorts are shown graphically. The microstructure of zinc retorts has been examined by A. Scott,[18] and it is shown that the blue constituent which is so conspicuous in the fracture of used retorts is a spinel, $ZnAl_2O_4$.

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[12] *J.*, 1920, 6R.

[13] *J.*, 1920, 300R, 395R.

[14] *J.*, 1920, 113R.

[15] *Eng. and Min. J.*, 1920, **110**, 405 ; *J.*, 1920, 660A.

[16] *Metall u. Erz*, 1919, **16**, 191, 219, 363 ; *J.*, 1920, 66A, 300A.

[17] *Metall u. Erz*, 1920, **17**, 137 ; *J.*, 1920, 412A.

Several papers on the theoretical aspects of zinc reduction and distillation have appeared. E. Jänecke[19] discusses the phase equilibria in the retort, and points out that the reactions are slower than might be expected, owing to the sluggish character of reactions involving two solid phases. The vapour pressures of zinc and cadmium have been determined over a range of temperatures by H. Braune,[20] and the results expressed in formulæ, which will be found useful in determining the separation of the two metals in the distillation process. M. Lemarchands[21] shows that the reduction of zinc oxide by carbon may take place directly, without the intermediate formation of carbon monoxide. The amount of carbon entering into the reaction is intermediate between that required for the production of monoxide and of dioxide, owing to the fact that the reaction $ZnO+CO=Zn+CO_2$ takes place with a higher velocity than the reaction $CO_2+C=2CO$.

Many experiments continue to be made with the object of employing the electric furnace for the reduction of zinc ores in place of the retort furnace. According to R. M. Keeney,[22] two plants are in successful operation in Sweden, largely engaged, however, in the smelting of dross. Although the excessive production of blue powder, which was the first difficulty of electric smelting, is said to have been completely overcome, the process has not yet become a commercial success in the United States. A 1000 kw. carbon resistance furnace has been installed for the melting of cathodes from an electrolytic zinc plant, and has been operated with a power consumption of 70–80 kw.-h. per ton of metal, and a loss in melting of only 0·024%. For this purpose the furnace should be well adapted. A new type of electric resistance furnace has been described by C. H. Fulton,[23] having been erected on a commercial scale at East St. Louis, Ill., the principle being that of making the roasted ore or concentrates into briquettes with the necessary carbon, and using these briquettes as the resistance elements through which the heating current passes. The briquettes are made by heating the ground mixture to 250° C., adding molten pitch, and forming in a press into cylinders 9·25 in. in diameter and 22 in. long. These masses are then baked on cars at a temperature rising to 500° for the last part of a 6-hour period. The resistance falls rapidly when the coking temperature is reached. The finished briquettes are arranged in the furnace in twelve columns of three each, set within a circle and supplied with three-phase current, four columns being on each phase. Graphite blocks are used above and below for making the electrical connexions, but it is proposed to replace these by blocks made from the same mixture as the briquettes. The chamber enclosing the charge serves as a retort, and was heated in the experiments by radiation, but preheating by means of regenerative gas-firing is proposed. A large furnace has been designed, and the principle is considered to promise good results. The recovery of zinc in the form of oxide from an open-hearth steel furnace when galvanised scrap is used in the charge is described by R. W. Müller,[24] the gases being drawn through a tubular cooler by means of an exhauster, but the method does not offer a very favourable prospect.

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[18] *Trans. Ceram. Soc.*, 1918-19, 512; *J.*, 1920, 237A.

[19] *Metall u. Erz*, 1919, **16**, 247 ; *J.*, 1920, 492A.

[20] *Z. anorg. Chem.*, 1920, **111**, 109 ; *J.*, 1920, 548A.

[21] *Comptes rend.*, 1920, **170**, 805 ; *J.*, 1920, 238A.

[22] *Chem. and Met. Eng.*, 1920, **23**, 980.

[23] *Chem. and Met. Eng.*, 1920, **22**, 73, 130 ; *J.*, 1920, 193A ; *cf. Ann. Repts.*, 1919, **3**, 234.

The electrolytic zinc plant of the Judge Mining Co., Park City, Utah, is described by L. W. Chapman.[25] The ground concentrates are leached with acid liquor until the acidity is reduced to a value corresponding with 3 g. sulphuric acid per litre. Ferrous sulphate is added to bring the iron content to 0·3 g. per litre, and the addition of powdered lime then precipitates the whole of the iron, with practically the whole of the arsenic and antimony. The residue contains a considerable quantity of zinc, and is shipped to smelters for recovery of zinc, lead, and silver. The filtered solution is treated with zinc dust before electrolysis, and on passing to the tanks contains the following elements in grams per litre: zinc 60, cadmium 0·004, copper 0·003, manganese 0·4, antimony 0·001, arsenic trace. Stationary cathodes of rolled sheet aluminium are used, with chemical sheet lead anodes. The current density is 24·5 ampères per sq. ft. of cathode. The acidity of the solution leaving the last tank is 60 g. per litre. The plant produces about 9 tons of zinc daily.

The same author describes the plant of the Consolidated Mining and Smelting Co. of Canada at Trail, B.C.[26] This is capable of producing 75 tons daily, the concentrate being roasted as above and the product leached in two stages. The purified solution contains, in grams per litre, zinc 60, iron 0·02, copper 0·0005. Electrolytic lead is used for anodes, and the current density is 24·2 ampères per sq. ft. In both plants the cathodes are melted in reverberatory furnaces for casting. The success of an electrolytic process for the production of zinc depends on the efficient purification of the solution before passing to the electrolysing tanks, the thorough removal of other metals being essential.

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[24] *Stahl u. Eisen*, 1920, **40**, 1193; *J.*, 1920, 693A.

[25] *Chem. and Met. Eng.*, 1920, **22**, 537.

[26] *Chem. and Met. Eng.*, 1920, **23**, 227.

The metallurgy of tungsten, which has only recently received any attention in the scientific press, has lately been the subject of several publications. Whilst by far the greater part of the tungsten produced finds application in the steel industry, the addition of the metal to non-ferrous alloys has been tried to a limited extent, whilst the manufacture of ductile tungsten for electrical purposes, although only accounting for a small fraction of the output, presents metallurgical features of extraordinary interest. The occurrence of the ore in Burma is described by J. C. Brown,[27] who remarks that the mechanical concentration of wolframite is difficult, owing to the fact that the mineral cleaves into thin plates like mica, and so slimes readily. The High Speed Alloys Co. now uses magnetic concentrators of the Ulrich type. The methods adopted for the reduction of the ore in France are described by C. Matignon.[28] Ferro-tungsten is manufactured in the electric furnace, whilst powdered tungsten is prepared from purified wolframite, the iron and manganese of which are removed by extraction with sulphuric acid. Reduction of the tungstic acid is carried out in graphite crucibles. The English method of preparing pure tungsten powder, as carried out at Widnes, is described by J. L. F. Vogel,[29] the mineral in this case being decomposed by means of soda. Great improvements have recently been effected in the consumption of fuel in this process, only half as much coal being used as was the case four years ago. The world's situation in regard to tungsten is reviewed by the same author.[30] This is a field in which British progress has been very satisfactory, this country having been entirely dependent on imported tungsten before the war, although the ore was mainly derived from British possessions, whilst at the present time the entire requirements of pure tungsten are supplied at home, and metal is available for export. The manufacture of ductile tungsten has been briefly described by the writer,[31] and a full description, with drawings of the plant, is given by C. H. Jones.[32] The ore is roasted with sodium carbonate and leached with water, and the clear solution of sodium tungstate is then precipitated with calcium chloride. The well-washed precipitate of calcium tungstate is decomposed by hydrochloric acid, and the residue repeatedly washed. This tungstic acid, 99·53% H_2WO_4, is not sufficiently pure, and has to be further purified by extraction with warm ammonia and evaporation of the solution of ammonium paratungstate to a paste, followed by decomposition with nitric acid. After ignition, the tungsten trioxide has a purity of 99·95%. The greatest trouble is found in accidental contamination with silicates etc. from such sources as chipping of enamel linings. The oxide is reduced by hydrogen at 1200° C., being placed on nickel trays in electrically-heated silica tubes. The powder is compressed hydraulically, and transferred to the sintering furnace, in which an atmosphere of hydrogen is also maintained. The swaging furnace, also filled with hydrogen, is built up of alundum tubes, the temperature ranging from 1100° to 1500°. In addition to lamp filaments and other fine wire, the metal is rolled into strip, and also made into contact buttons. For the latter purpose, the thick rod is cut into slices by means of abrasive wheels with a rubber binder, and each slice is then brazed to a steel stud by interposing a thin sheet of copper and heating in hydrogen until the metals unite. The thin coating of copper formed by volatilisation is removed electrolytically. A similar process is used in the manufacture of molybdenum.

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[27] *J.*, 1920, 45T.

[28] *Chim. et Ind.*, 1920, 3, 277, 422.

[29] *J.*, 1920, 299R.

[30] *J.*, 1920, 103R.

[31] *J.*, 1920, 299R.

[32] *Chem. and Met. Eng.*, 1920, 22, 9; *J.*, 1920. 150A.

ALLOYS.

Brasses, on account of their great industrial importance, have been the subject of numerous investigations. A series of experiments on the influence of gases on brass, conducted by T. G. Bamford and W. E. Ballard,[33] indicates that overheating during melting is not dangerous, provided that the furnace is of the ordinary coke-fired type, although it is to be avoided on account of the resultant high loss of zinc, but that allowing to cool until the temperature of the metal is only 40° above the solidus is almost sure to cause unsoundness. Cadmium, in quantities up to 0·74%, the limit of solid solution, is without effect on the mechanical properties of 70:30 brass, according to L. Guillet,[34] but higher cadmium lowers the elongation. The coefficient of equivalence is 0·7, that is, 1% of cadmium has the same effect on the structure as 0·7% of zinc. The same author has examined the effect of several other elements on brass. Cobalt and silver have comparatively little effect, chromium is undesirable, and gold merely replaces copper.[35] Nickel has been the object of a more extended study by the same authority,[36] and it is shown that when the copper falls as low as 40% or less, the nickel being about 15%, strong alloys are obtained, with an elongation of 18–45%. These alloys are malleable when hot, and closely resemble the nickel-silvers in colour and resistance to oxidation. Hot compression tests have been made on a number of brasses by F. Doerinckel and J. Trockels.[37] It is stated that the hot-working of α-brasses has been long known, but regarded as a trade secret. Tombak with 12% and 15% of zinc, and brass with 29% and 33% of zinc could be forged at 800° C., whilst the αβ-brasses became fully plastic at 700°. Hardness tests at high temperatures by A. Mazzuchelli[38] show that 20% brass withstands the highest temperature before softening.

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[33] *J. Inst. Metals*, 1920, **24**, 155; *J.*, 1921, 84A.

[34] *Rev. Mét.*, 1919, **16**, 405; *J.*, 1920, 157A.

[35] *Comptes rend.*, 1920, **171**, 172; *J.*, 1920, 601A.

[36] *Comptes rend.*, 1920, **170**, 460; *J.*, 1920, 269A.

Problems connected with the manufacture of brass cartridge cases have led to the publication of several interesting papers. H. Moore and S. Beckinsale[39] have determined the conditions under which internal stress in 70:30 brass may be removed by low-temperature annealing, and find that the greater the initial Brinell hardness of the brass the lower is the temperature and the shorter the time required to bring about an appreciable reduction of hardness. When the hardness produced by cold working does not exceed 165, annealing for one hour at 275° C., or for five hours at 250° C., will remove all injurious internal stress without causing loss of hardness. A temperature of 100° C., even when continued for many weeks, appears to be without effect on internal stress. The authors also observed the remarkable increase of hardness which marks the first stage of annealing at low temperatures, this increase being now a well established fact. Spun cups were used for the experiments, this form of cold working being very severe. The characteristics of cracks in brass cartridge cases are described by M. von Schwarz.[40] A number of these cases developed cracks at the junction of the base and side, starting from the inside and proceeding diagonally to the angle. The microscope showed excessive cold working at this point, and measurements of hardness by the Brinell and scleroscope methods showed regions of unequal hardness, reaching a maximum close to the cracks. The scleroscope was found to be a more sensitive means of recognising such differences than the Brinell machine. The maximum Brinell figure obtained was 178. E. H. Schulz[41] has examined similar brass cases, and concludes that cracking occurs when the cold working is not uniform, so that regions of unequal hardness are in immediate contact. Minute cracks are often present when the cartridge case is first made, and whilst these may to some extent relieve the stress, they may bring about fracture when the brass is subjected to shock by acting as notches and so intensifying the stress.

The hot-working brasses of the 60:40 type have also been studied.

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[37] *Z. Metallkunde*, 1920, **12**, 340.

[38] *L'Industria*, 1920, **34**, 71.

[39] *J. Inst. Metals*, 1920, **23**, 225; *J.*, 1920, 369A.

[40] *Z. Metallkunde*, 1920, **12**, 1.

[41] *Z. Metallkunde*, 1920, **12**, 263.

H. M. Brayton[42] describes the effect of heat treatment on two alloys of this class, A containing 60·58% copper and 0·75% tin, and AA 56·17% copper, 2·53% lead, and 0·06% tin, the remainder being zinc. The rods were drawn to $\frac{17}{32}$ in., annealed, and cold-drawn through a $\frac{1}{2}$ in. die. Such metal has a Brinell hardness of about 130. The tensile strength is increased by quenching from temperatures about 550° C., owing to partial conversion of a into β; but above 700° the strength falls off rapidly, owing to grain growth. A definite elastic limit is found at about 20% of the ultimate tensile strength, but there is no indication of a yield-point. The curves contained in the paper show the most suitable temperatures of annealing or quenching in order to obtain a given combination of strength and ductility. The present writer[43] has also studied the properties of rolled, drawn, and extruded 60:40 brasses, especially in regard to their machining quality, and finds that the greatest ease of machining is obtained when the copper, both actual and apparent, approaches most closely to 60%, and that lead is the only metal which may be added with advantage Brasses which are hard to machine usually contain tin, iron, or other hardening metals, or else are too high in zinc content, so that the proportion of the β constituent is large. The best brasses have a fibrous structure, and in the case of extruded rods this involves extrusion at a relatively low temperature under a high pressure. It is shown that there is no relation between the Brinell hardness and the machining quality. Attempts to obtain castings of high tensile strength are described by N. J. Maclean.[44] Experiments with a variety of added metals led to disappointing results, but finally an alloy containing 60% copper, 34·0 zinc, 3·0 nickel, 2·0 iron, 0·25 lead, 0·5 manganese, and 0·25 phosphor-tin was adopted, this alloy giving castings in sand moulds which could be depended on to give an elastic limit of 10 tons, breaking load of 20 tons, and elongation 15%. Exception was taken to these figures in the discussion, and it was stated by several speakers that much better results could be obtained from well-known non-ferrous alloys and that equally good figures could be obtained with Admiralty gun metal. The discussion turned largely on the difference between the tensile results obtained from a test piece cast in a selected position and those given by a portion of the casting, the object of the author being to know the strength of the weakest part of the casting. A paper by W. B. Weeks[45] mentions that a 60:40 brass containing 2% nickel and 3% manganese will give 15 tons elastic limit, 32–36 tons breaking load, and 15% elongation, whilst another high-tensile brass will give, from any part of the casting, 20 tons elastic limit, 40 tons breaking load, and 20% elongation. This paper contains a useful account of brass foundry practice in Vickers' works at Barrow.

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[42] *Chem. and Met. Eng.*, 1920, **22**, 211; *J.*, 1920, 269A.

[43] *J.*, 1920, 216T.

[44] *J. Inst. Metals*, 1920, **23**, 193; *J.*, 1920, 301A.

[45] *J. Inst. Metals*, 1920, **24**, 67.

There is little doubt that the results obtained from special brasses and similar alloys in the average foundry are far inferior to those which it is possible to obtain from alloys of the same nominal composition. Rigid analytical control, careful selection of scrap, and attention to casting temperatures, enable non-ferrous alloys of quite surprising strength and ductility to be made regularly in the foundry without resort to unusual or expensive combinations of metals. The publication of such papers as those just mentioned will be of great service in drawing attention to the possibilities of the brasses and bronzes in the hands of skilled metallurgists. In determining the nature and amount of the third metal to be added in the making of special brasses, a knowledge of the ternary equilibrium diagram is essential, and W. Campbell[46] has studied the behaviour of tin, following up the work of Hudson and others, and has aimed at defining the boundary between the ductile "naval brasses," which are made up of the *a* and *β* constituents, and the "gun metals," composed of *a* and eutectoid, and exhibiting brittleness. Within the usual limits, the quantity of tin which may be safely added is inversely proportional to the percentage of copper. The difference of properties of cast and electrolytically deposited brass is described by F. Sauerwald,[47] but the results are mainly of theoretical interest.

The elastic properties of the ordinary non-ferrous alloys are not often studied, but a paper by G. F. Comstock[48] shows that interesting results may be obtained by tracing the stress-strain diagrams for copper alloys. Cast specimens were used, held in an Olsen machine by grips with spherical seatings, and the deformations were measured by means of a strain gauge. The alloys examined were 10% aluminium bronze containing iron, and 88 : 10 : 2 gun metal, both of which show well-defined limits of proportionality which could be utilised for commercial purposes. There is no definite relation between these limits and the yield-points or tensile strengths, and it is suggested that the common practice of accepting the yield-point as representing the practical elastic limit should be abandoned.

The light alloys of aluminium have assumed increased importance as the result of war experience, especially with aircraft, and their investigation has occupied many workers during the last year or two. The peculiar behaviour of some of them after heat treatment has been the cause of much speculation, but its causes have not been completely elucidated. The metallography of the light alloys containing copper and magnesium, which are among the most important of the class, is described by P. D. Merica, R. G. Waltenberg, and J. R. Freeman.[49] The solubility of the intermetallic compounds and impurities has been determined, and an attempt made to fix the position of the curves of solubility in the solid state, but the photographic work is poor, and the investigation is not to be compared with those which have been conducted at the National Physical Laboratory in recent years. A paper on a similar subject by P. D. Merica, R. G. Waltenberg, and A. N. Finn[50] shows that the alloys with copper and magnesium are decidedly superior to others examined in regard to tensile properties, and that they are more strikingly improved by heat treatment than, for instance, the corresponding alloys containing nickel and magnesium, the treatment also improving the resistance to corrosion by a salt spray. Hard-rolling and annealing completely alter the relative order of resistance of a series of alloys. A careful study of the mechanical and physical properties of a number of light aluminium alloys by W. Fraenkel and R. Seng[51] indicates that the property of being improved by heat treatment is peculiar to those alloys which contain magnesium. The authors are inclined to consider that the increase of strength is due to the formation of a chemical compound within the homogenous solid solution, the evidence for this view being taken chiefly from measurements of electrical conductivity. The resistance increases with time in a manner almost exactly corresponding with a unimolecular chemical reaction. The changes of density and specific heat are insignificant. A knowledge of the constitution of the alloys of aluminium and magnesium is obviously of importance for the right understanding of the commercial alloys, and the constitutional diagram has been very carefully worked out by D. Hanson and M. L. V. Gayler.[52] The micrographic work is excellent, and although the form of the liquidus and solidus in the middle part of the system places difficulties in the way of determining the exact formula of one of the intermetallic compounds, there can be no doubt that the diagram is essentially correct. Particulars of some of the most useful of the aluminium alloys are given by W. Rosenhain.[53] The so-called 3:20 alloy, containing 3% copper and 20% zinc, attains in the hot-rolled condition a tensile strength of 26–27 tons, with an elongation of 18%, and has been found of value in the construction of girders for rigid airships. For general castings, such as crank cases and carburettors, an alloy with 2·5%

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[46] Amer. Soc. Test. Materials, June, 1920; *Chem. and Met. Eng.*, 1920, **22**, 1191; *J.*, 1920, 629A.

[47] *Z. anorg. Chem.*, 1920, **111**, 243; *J.*, 1920, 661A.

[48] *Chem. and Met. Eng.*, 1920, **22**, 1113.

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[49] *Bureau Stand. Sci. Paper No.* 337.

[50] *Bureau Stand. Tech. Paper No.* 132 ; *J.*, 1920, 454A.

[51] *Z. Metallkunde*, 1920, **12**, 225.

[52] *J. Inst. Metals*, 1920, **24**, 201.

[53] *J.*, 1920, 233R.

copper and 12·5% zinc has given good results, the tensile strength of chill castings being 12 tons. Alloys containing nickel with magnesium and copper have proved most successful for pistons and cylinders working at high temperatures, and have greatly simplified the construction of engines for aircraft.

The rate at which thin sheet copper will dissolve in molten aluminium has been determined by R. J. Anderson,[54] who concludes that copper may be added in small quantities in this form, but that when larger quantities are being made it is preferable to add a 50:50 alloy. The latter should be well stirred during its preparation, and cast in a chill mould, otherwise excessive segregation may occur. Melting and rolling practice in the manufacture of aluminium alloys is dealt with in a series of articles by R. J. Anderson and M. B. Anderson.[55] Gas or oil-fired reverberatory furnaces are mostly used for melting in America, but electric resistance furnaces are being tried. The methods of rolling are fully described.

Two papers describing the properties of Monel metal, the alloy of nickel and copper obtained by direct smelting of the Sudbury ores, have been published. H. R. Williams[56] lays stress on its strength at high temperatures, which makes it suitable for turbine parts etc. The coefficient of expansion is 0·00001375, and its specific gravity in the cast state 8·87. Average tests on castings give a yield-point of 16·5 tons, a tensile strength of 32 tons, and an elongation of 34%. According to J. Arnott,[57] rolled and annealed rods give a yield-point of 20–22 tons, a tensile strength of 38–39 tons, and an elongation of 47%, the properties being little changed by annealing up to 700° C. The tensile strength is only about 5 tons less at 375°. For turning, high speed steel should be used, a light cut being taken at a high speed. Electric furnaces of the arc type are preferable to crucibles for melting. The author does not claim so high a tensile strength for the cast metal as do American writers, regarding 20–25 tons as a normal value. Magnesium is the best deoxidiser, manganese being less successful than with pure nickel.

Alloys containing zinc with relatively small quantities of other metals were not very important before the war. Owing to the shortage of copper in Germany, such zinc alloys were largely used in munitions as substitutes, under such names as "war bronze." It does not appear that they ever proved to be very satisfactory, and the disposal of the stocks has presented some difficulty. There have been two studies of the constitution of the ternary system zinc-copper-aluminium, that of V. Jareš,[58] extending over the whole system except the region near to the copper angle, and being based on thermal and mechanical observations, almost without microscopical examination, whilst the investigation of W. Rosenhain, J. L. Haughton, and K. E. Bingham[59] makes fuller use of the microscope, but also includes an extensive series of mechanical tests. According to these authors, an alloy containing 3% copper and 6–15% aluminium shows remarkable strength in the cast condition. The rolled alloys containing more than 0·5% aluminium together with copper undergo deterioration in course of time, so that for engineering purposes the binary alloys are to be preferred. Curiously abnormal properties were observed in the case of the ternary eutectic, which is quite brittle if bent rapidly, but may be bent slowly through an angle of 180°, thus resembling pitch rather than a crystalline metal. Jareš finds that alloys containing 5–8% copper and 1–3% aluminium, the one metal being high when the other is low, give the best results, castings only being considered. These mixtures were largely used in Germany for fuse bodies, and also for many engineering parts in place of brass or gun metal. Their use led occasionally to serious difficulties. For example, a screw socket of "war bronze" is described by O. Bauer[60] as having been used on a boiler, the composition of the alloy being copper 4·85, aluminium 2·19, lead 0·92, tin 0·15, iron 0·03%. This was completely decayed by electrolytic action, a skeleton of copper-rich crystals remaining. An alloy of very similar composition was used for fixing the blades of a steam turbine, and after a few days the mass became entirely brittle owing to chemical action.[61] It is clear that such mixtures are not likely to find any extensive application in future. The problem of recovering the useful metals from them is not an easy one, as they cannot be used for making brass without first removing the aluminium. Blowing air through the molten metal was tried without success, and according to J. Czochralski and E. Lohrke[62] the most successful treatment consisted in fusing with sodium nitrate, preferably with the addition of sodium chloride and potassium carbonate. The nitrate being scarce, potassium perchlorate was used as a substitute. The addition of 2% of tungsten to the alloys of zinc containing aluminium is stated[63] to give good working properties and resistance to corrosion.

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[54] *Chem. and Met. Eng.*, 1920, **23**, 575, 735, 883; *J.*, 1920, 786A.

[55] *Chem. and Met. Eng.*, 1920, **22**, 489, 545, 599, 647, 697.

[56] *Amer. Machinist*, 1920, **51**, 509.

[57] *J. Inst. Metals*, 1920, **23**, 545.

Reference may be made to a few papers on the subject of bearing metals. The distribution and character of the hard crystals in alloys of tin with copper and antimony has been studied by O. F. Hudson and J. H. Darley.[64] The hardening of lead by metals other than antimony has also received attention, partly again in consequence of war scarcity of essential metals. Barium has been used in several places, and J. Czochralski and E. Rassow[65] show that the hard crystals consist of the compound Pb_3Ba. One % of calcium hardens lead, according to C. O. Thieme,[66] as much as 10% of antimony. Mercury exerts a hardening influence in quantities up to 7%. Other alloys in which sodium is present together with tin or mercury are described by T. Goebel.[67]

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[58] *Z. Metallkunde*, 1919, **10**, 1; *J.*, 1920, 67A.

[59] *J. Inst. Metals*, 1920, **23**, 261; *J.*, 1920, 370A.

[60] *Z. Metallkunde*, 1920, **12**, 129; *J.*, 1920, 661A.

[61] M. von Schwarz, *ibid.*, 262.

[62] *Z Metallkunde*, 1919, **11**, 53; *J.*, 1920, 630A.

[63] *Chem. and Met. Eng.*, 1920, **22**, 9.

Papers on the mechanism of cold working have been numerous, but are mostly of scientific interest only, the application of theory to practice being still imperfect. Reference should be made, however, to a further paper on the properties of cold-drawn copper wire by W. E. Alkins.[68] The discontinuous change of properties when a certain stage in the drawing has been reached, described a few years ago, has now been fully confirmed, and unless there should prove to be some change in the character of the drawing process at this point, a remarkable transformation of the metal has been demonstrated. Experiments on the rolling of copper by F. Johnson[69] show that rolling is a much more irregular and uncontrollable process than drawing, so that smooth curves illustrating the change of properties cannot be obtained. There is some indication, however, of the same discontinuity as that recorded by Alkins. An important paper on grain growth and recrystallisation in cold worked metals has been contributed by H. C. H. Carpenter and C. F. Elam.[70] These authors were fortunate enough to find an alloy, consisting of tin with only 1·5% of antimony, which has the property of showing distinct boundaries on a polished surface at each stage of grain growth, so that the process can be followed with ease. The experiments throw much light on this problem, which is still so obscure.

CORROSION.

The subject of the corrosion of metals and alloys continues to receive much attention, and although the theory of the phenomena remains in a remarkably confused condition, there is now no lack of careful observations and experiments on which conclusions may in course of time be based. The most important contribution to the subject during the past year is the Fifth Report to the Corrosion

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[64] *J. Inst. Metals*, 1920, **24**, 361; *J.*, 1921, 85A.

[65] *Z. Metallkunde*, 1920, **12**, 337.

[66] *J. Ind. Eng. Chem.*, 1920, **12**, 446; *J.*, 1920, 454A.

[67] *Z. Ver. deuts., Ing.*, 1919, 424; *J.*, 1920, 116A.

[68] *J. Inst. Metals*, 1920, **23**, 381; *J.*, 1920, 368A.

[69] *Ibid.*, 443; *J.*, 1920, 369A.

[70] *J. Inst. Metals*, 1920, **24**, 83; *J.*, 1921, 85A.

Committee of the Institute of Metals, a body which has already rendered most valuable services in this connexion.[71] The latest communication deals in the main with the same points as the Fourth Report, but with the addition of more evidence, and with increased definiteness. The authors have made further investigations of the surface layer on drawn condenser tubes. This layer may be completely stripped off the tube by the action of ammonium chloride, and proves to be highly resistant to the usual corroding agents. The problem of preserving condenser tubes thus becomes, to a great extent, one of maintaining this surface layer in an unbroken condition. It is regarded as structureless, and as more resistant than the crystalline alloy, whilst the amorphous intercrystalline material is regarded as less resistant even than the crystals. Such a condition is difficult to picture in the light of any possible hypothesis of cold-working, but the existence of the superficial layer is definitely established, and the fact that it can be stripped from brass, copper, and phosphor-bronze is one of great importance. Attempts to strip a similar layer from nickel-copper tubes have failed, and it is suggested that these tubes are very thoroughly cold-worked throughout their thickness. The various types of corrosion which are actually encountered in condenser tube practice are discussed in detail. Rapid general thinning is mostly confined to fresh-water installations, and is attributed to acids, in which case it may be prevented by careful neutralisation. A remarkably low concentration of acid suffices to bring about such thinning. Local attack is usually much more serious, and also more difficult to deal with satisfactorily. The authors have been unable to trace the formation of pits to local differences in the electrolytic character of the metal, and attribute the attack to the influence of deposits of basic salts of copper and zinc, as to the production of which they bring forward much interesting evidence. The formation ot minute quantities of cupric chloride solution of comparatively high concentration under basic deposits is considered to be responsible for much intense local action. The copper which is found on the surface after corrosion, or in the form of plugs where deep pitting has taken place, is stated to be in all cases of secondary origin, the copper and zinc first passing into solution together, and the copper being subsequently re-deposited in its original position. Although this suggestion has been welcomed by most of those who have taken part in the discussion, it is by no means easy to picture the mechanism of the reaction, and the writer remains of the opinion that the older view, that the zinc is preferentially dissolved, more nearly represents the facts. Is it suggested that in the parting of gold bullion the gold dissolves completely in the parting acid together with the silver, and is then re-deposited as a pseudomorph? The two cases are precisely parallel.

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[71] G. D. Bengough, R. M. Jones, and R. Pirret, *J. Inst. Metals*, 1920, **23**, 65; *J.*, 1920, 369A.

The difficulty of the subject is shown by the remark of the authors that if two batches of condenser tubes are taken, one of which is known to undergo pitting readily in use and the other not, the composition being apparently identical, the differences in behaviour persist after annealing, so that their cause is quite unknown. A trial experiment seemed to show that the differences are not due to unequal casting temperatures. Treatment of the tubes by previous oxidation has little effect on local pitting.

In the course of the discussion on the Report, Dr. Rosenhain remarked that the stresses in the inner and outer portions of a cold-drawn tube will differ in sign, whilst it is well known that certain chemical agents, such as mercury salts, separate the crystals of a metal in tension, but not in compression. This point is of importance.

Another question dealt with in the Report is that of the limits of electrolytic protection, which are found to be more restricted than is commonly supposed to be the case. Local action, especially when due to cupric chloride, proceeds independently of a protecting current, but the application of a current during the early part of the life of a tube may result in the formation of a film of calcium carbonate which will materially assist the prevention of attack.

It was the experience of all naval vessels operating during the war in shallow, sandy waters, that condenser tube troubles were much more serious than under ordinary conditions, the erosive action of the sand contributing greatly to the destructive action of the sea water. Notes on the causes of tube failures have been published by G. B. Allen,[72] who remarks on the large proportion of cases in which thinning takes place at the inlet end, and shows how imperfect centring and fitting may cause eddies where air may accumulate, and means of obviating this difficulty were suggested in the discussion. Stagnant water in fitting-out basins etc. is responsible for much injury to condensers. German naval experience in this field is described by Schulz.[73] The German specification for tubes was less rigid than that of the British Navy, and a larger proportion of failures occurred before the war. Large ships employed an alloy of 98% copper and 1·45% tin, whilst torpedo boats used the 70 : 30 and 70 : 29 : 1 alloys. During the war the scarcity of copper and tin led to the use of brass tubes on all vessels, an alloy with 62% copper being adopted, the tubes being formed either by hot rolling or extrusion, followed by cold-drawing. After annealing at 650°–700°, the tubes were cleansed in soda, followed by a bath of salt-cake, and then tinned inside and outside.

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[72] *J. Inst. Metals*, 1920, **24**, 285.

[73] *Z. Metallkunde*, 1920, **12**, 149.

For this purpose an alloy of 70 tin and 30 lead was used, but the shortage of tin led to this being replaced by 90 lead and 10 tin, which was more difficult to apply. Scarcity of copper led to several vessels being fitted with iron condenser tubes, coated with this lead alloy, whilst a coating of bakelite varnish on brass was also found to be fairly resistant. A curious method of protection, adopted by some firms, but not by the Navy, consisted in rolling or pressing iron filings into the surface of the brass. Such a coating is, however, almost impossible to renew. It is interesting to note that English brass tubes, supplied to merchant vessels, were taken as the standard at which the manufacturers were to aim. The defects observed are generally of the same character as those described by the Corrosion Committee, and it is clear that design etc. has as much share in determining the results as the composition of the metal of which the tubes are constructed. A paper on the same subject by O. Lasche[74] attributes numerous failures (mostly, however, on land stations) to stray currents, and favours the use of protective currents, or even of zinc plates at certain points, such as at the entry of polluted water in a pumping plant. The limited range of the protective action exerted by a neighbouring anode was pointed out in the discussion by O. Bauer. Changes in the composition of the tubes appear to have had very little influence in determining the proportion of failures. The data included in the papers just mentioned are sufficiently extensive to make a comparison with those collected by the English Committee of value.

Tests have been made by P. D. Merica and R. W. Woodward[75] to determine the safe stress to which wrought $\alpha\beta$-brass ("manganese bronze") may be subjected while exposed to corrosive agents. In water and moist air it was found that no specimen examined failed in two years under stresses below the elastic limit, whilst some bars even withstood for that time stresses which caused slight permanent set. The test pieces had been annealed at low temperatures before the experiments.

Other experiments on the corrosion of brass and bronze have been made, without greatly advancing our knowledge. The influence of various dilute solutions of electrolytes on the corrosion of brass has been examined by J. H. Reedy and B. Feuer,[76] and B. Feuer[77] has made measurements of the fall of potential between the surface of the metal and the solution, using an auxiliary electrode. The order of potential thus obtained is evidently not a measure of the order of corrodibility, since the physical conditions of the surface film and of the products of corrosion do not enter into the experiment.

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[74] *Ibid.*, 1920, **12**, 161.

[75] *Proc. Amer. Soc. Testing Materials*, 1919, **19**, ii., 278.

[76] *J. Ind. Eng. Chem.*, 1920, **12**, 541; *J.*, 1920, 519A.

[77] *Chem. and Met. Eng.*, 1920, **22**, 1197; *J.*, 1920, 630A.

The corrosion of aluminium has also received attention, the most important paper being one by R. Seligman and P. Williams,[78] dealing with the action of hard industrial waters. Immersion in most waters leads at first to superficial etching, gas being evolved and aluminium hydroxide formed, the action then being brought to a stop by the production of a film of calcium carbonate. Local pitting is much more serious, and tends to persist after having once begun. Neither action takes place in the absence of oxygen. The action is clearly electrolytic, and is connected with the presence of areas of different potential on the surface of the metal, although on hammering selected spots on a sheet of annealed aluminium it cannot be said that the pits or blisters appear preferentially on the hammered areas when corrosion sets in. Small quantities of hydrogen peroxide, itself a product of the action of tap water on aluminium, greatly accelerate the corrosion. Blistering occurs when the water gains access to one of the minute cavities always present in the metal, and the accumulation of the products of corrosion within the cavity leads to the formation of bulky aluminium hydroxide, which forces the laminæ apart. The removal of bicarbonates by boiling the water greatly diminishes its corrosive action, whilst complete immunity from pitting is obtained by the addition of 0·01% of a nitrate. A convenient and efficient means of protection was found in sparingly soluble chromates, such as those of barium or strontium, mixed with gelatin and hardened by formaldehyde, so that the chromate was given up slowly and continuously to the water. The application of an external E.M.F. also protects the metal. The authors fully recognise the inadequacy of loss of weight tests. The influence of concentration and time on the solvent action of various electrolytes on aluminium is described by G. H. Bailey.[79] At high temperatures the action may continue to a quite remarkable extent. Thus, in $N/1$ hydrochloric acid at 95° C., the action proceeds until the viscous solution corresponds approximately with the formula $Al_2(OH)_5Cl$, after which turbidity appears, and at last a bulky precipitate of a very basic chloride is formed, so that a small quantity of acid can dissolve a relatively large quantity of metal. Some aluminium alloys, especially those containing copper, have the property of forming a resistant film in the early stages of corrosion, and protection is best sought in this direction. Very efficient protection is claimed by L. von Grotthuss,[80] who makes the aluminium the anode in a bath containing a sulpho-compound of molybdenum. A fine brown deposit is formed, which is perfectly flexible and highly resistant to corrosion. The protection of metals in general by processes of electrolytic oxidation, described fully by L. Revillon,[81] may be mentioned in this connexion. The valve action of aluminium anodes is discussed by A. Smits.[82]

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[78] *J. Inst. Metals*, 1920, **23**, 159 ; *J.*, 1920, 301A.

[79] *J.*, 1920, 118T.

[80] *Metall u. Erz*, 1920, **17**, 39 ; *J.*, 1920, 301A.

The action of water on lead has been further studied by J. F. Liverseege and A. W. Knapp.[83] Using faintly alkaline natural waters, a sheet of bright lead was exposed to the attack of water with free access of air. Very erratic results were obtained, as air bubbles, dust particles, and other apparently unimportant factors exert a quite considerable influence on the extent of the corrosion. The action is checked by the addition of calcium bicarbonate to the water. Free carbon dioxide increases the rate of solution, and alters the character of the action. In the soft water, the action is essentially due to dissolved oxygen. A series of experiments on the suitability of different qualities of lead for use in chemical plant has been made by D. W. Jones,[84] who shows that whilst the purest lead is probably the best, the addition of copper may sometimes be advantageous. The copper is easily introduced in melting in the form of a 50% alloy. The simultaneous presence of copper and antimony is harmful. The inter-crystalline attack which is characteristic of the action of some electrolytes on sheet lead is attributed by H.S. Rawdon[85] to the presence of impurities at the grain boundaries. It should be remembered, however, that this action may be observed with the purest assay lead.

Alloys of copper with iron and aluminium have been tested for acid-resisting properties by O. L. Kowalke.[86] These alloys, as manufactured for use in chemical plant, contain about 10% of aluminium and 3–3·5% of " iron alloy," the composition of which is not stated. They resist organic and sulphuric acids well, but are readily attacked by hydrochloric or nitric acid.

Closely allied to the subject of corrosion is that of inter-crystalline brittleness in metals, due to chemical action. H. S. Rawdon and S. C. Langdon[87] have described brittleness in copper, caused by immersion in a bath of molten salt, a process often employed to soften and clean the metal. The copper is in contact with iron or steel, so that it becomes the cathode in an electrolytic circuit, and the inter-crystalline cracks found in the exterior layers are attributed to the formation of metallic sodium. The interior is not rendered brittle, and no effect is observed when the copper is made the anode instead of the cathode.

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[81] *Rev. Mét.*, 1919, **16**, 257 ; *J.*, 1919, 907A.

[82] *Proc. Acad. Sci. Amsterdam*, 1920, **22**, 876 ; *J.*, 1920, 630A.

[83] *J.*, 1920, 27T.

[84] *J.*, 1920, 221T, 255T.

[85] *Min. and Met.*, Feb., 1920.

[86] *Chem. and Met. Eng.*, 1920, **22**, 37 ; *J.*, 1920, 158A.

[87] *Bureau Stand. Techn. Paper, No.* 158 ; *cf. J.*, 1920, 158A.

In all investigations of this kind, the microscope proves to be a most powerful instrument of research, and the progress of metallurgical knowledge is intimately bound up with the improvement of methods of microscopical technique. An important collection of papers on the microscope, dealing largely with its applications to metallurgy, both in its scientific and its industrial aspects, was contributed to the Faraday Society symposium at the beginning of the year.[88] An interesting account of the history of metallography was given by C. T. Heycock, whose own researches with F. H. Neville did so much to establish the value of the method, in his presidential address to the Chemical Section of the British Association.[89]

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[88] *Trans. Faraday Soc.*, 1920, **16**, Pt. 1; *J.*, 1920, 34R.

[89] *J.*, 1920, 285R.

ELECTRO-CHEMICAL AND ALLIED INDUSTRIES.

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The period covered by last year's report showed a general and pronounced decline of the industrial prosperity enjoyed during the war. At the end of the war it was still uncertain when and on what basis the relation between supply and demand would ultimately become stabilised under normal peace conditions. During the year now under review, there has been no sign of any industrial improvement, and the general depression has steadily advanced and has now reached a critical stage. Owing to the nebulous state of political and economic conditions, there has been considerable reluctance to finance fresh industrial enterprises either at home or abroad. The merits of newly invented processes are also impossible to judge at a time when the costs of fuel, raw material, and manufactured products are fluctuating, so that it is not surprising that this year has been remarkable for the lack of technical development and exploitation of new processes. There has certainly been some activity in the colonies to record, but so far this development has been mostly confined to the exploitation of water power as a necessary preliminary to the growth of electro-chemical industries. Nevertheless, in South Africa, Australia, and India, industrial progress has already commenced and may be expected to develop considerably as more electric power becomes available. In Sweden and Norway the year has been marked by serious trade depression, but in the latter country there are signs of recovery. In all other countries where electro-chemical industries have already been developed on a large scale, the same conditions prevail. This position has arisen owing to the depression in the iron and steel trades and to the cessation of the demand for the numerous electro-chemical products used in the manufacture of munitions. At the present time there is no prospect of any immediate revival in the industries affected, and until the world's markets are again opened, there seems little chance of operating the existing electro-chemical plants at anything approaching their full capacity.

STEEL.

There has been a further reduction of the world's output of electric steel in common with the restricted demand for high-grade alloy and carbon steel products. The unexpected depression of the motor-car industry has to some extent accounted for this situation in England, but the main causes are obviously wider, and are to be found in the general apathy of foreign and home markets. The table of statistics on p. 273 shows the amazing development of the electric furnace during the war period, and the subsequent reduction of output during the year 1919. The figures for 1920, when available, will show a further marked decline as a result of the immediate post-war requirements having been met during the previous year.

In the adjoining table are included statistica lreturns for several Continental countries which have only recently been obtainable. These permit a wider study to be made of the relative progress throughout the world during the war period. Unfortunately, the production of electric steel castings and ingots is returned as an aggregate figure for all countries except the United Kingdom and the United States of America. It is very striking to find that the production of steel castings in the latter countries showed no tendency to diminish during 1919, if allowance is made for the loss of output in England consequent upon the moulders' strike during the latter half of that year. These figures clearly bear evidence to the fact that the electric furnace has established a field of its own for foundry purposes, in which it is unlikely to be influenced by the competition of other processes. During 1920 the output of electric steel castings has only shown a small increase, owing to the recent depression in the motor and engineering industries of both this country and America. This, however, cannot be expected to last indefinitely, as heavy road transport has now become a permanent feature of national life. The future of electric steel foundries is, therefore, more promising than that of works producing ingot steel, in which case the electric furnace must produce in competition with the better classes of steel produced by the open-hearth process.

With regard to ingot steel, the electric furnace is now producing a large variety of plain carbon steels apart from the more complex alloy steels for which it was so extensively used during the war. The high cost of good hæmatite pig and high-class steel scrap has enabled the electric furnace to compete with the open-hearth furnace in the production of medium grade steels, but during the year this demand has been spasmodic.

In Sweden the electric furnace was used to supplement existing crucible plant for melting high-grade raw materials rather than for melting and refining common scrap; in a few cases furnaces are now being used for the latter purpose, but this method of steelmaking

Electric Steel Production.

	UNITED KINGDOM.		UNITED STATES.		FRANCE.	AUSTRIA-HUNGARY.	CANADA.	SWEDEN.	ITALY.	GERMANY & LUXEMBURG.
Year.	Castings.	Ingots.	Castings.	Ingots.	Castings & ingots.	Castings & ingots.	Castings & ingots.	Castings & ingots.	Castings & ingots.	Castings & ingots.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
1914	—	—	9000	15,000	—	19,844	—	1700	—	88,000
1915	2000	20,000	23,000	46,000	—	23,895	—	2200	22,000	132,000
1916	9288	39,968	43,000	126,000	45,000	47,247	30,000	6600	22,000	190,000
1917	15,600	105,000	65,000	240,000	54,000	47,152	37,000	10,600	37,000	220,000
1918	44,901	103,021	108,000	403,000	58,000	41,163	103,000*	13,000	47,000	240,000 (*a*)
1919	30,000	47,000	111,000	273,000	42,000	—	9000*	—	—	83,000 (*b*)

(*a*) Includes production of Lorraine and Luxemburg up to the end of October only.

(*b*) Includes estimated production for November and December, and excludes returns from Lorraine and Luxemburg.

* Ingots only.

is generally regarded in Sweden with considerable disfavour for making high quality carbon steels. A large number of the plants are now idle owing to the general depression of the steel trade, but at the same time a few units have recently been started and others are now in course of erection at various works where cheap hydro-electric power is available. Except at such favoured localities there is frequently a shortage of power for the development of the electric process, and even when sufficient power is available, the cost is often prohibitive. The induction furnace is still considered to have a use for melting special qualities of high grade raw materials, when there is no variation in the quality of material required. In this case there can be no marked refining action due to slag reactions, and any improvement in quality can only follow as a result of holding the liquid steel for a period, often amounting to some hours at a uniform temperature, while the necessary finishing alloys are added.

A noticeable feature during the year has been the growing adoption of the electric process in the Dominions. Australia and South Africa have already installed several units, but their requirements are not yet satisfied. In most cases the plants are used for the production of castings from the abundant and cheap supplies of scrap steel, especially for mining and railway work, and in the near future all these countries should be self-supporting and independent of foreign production. There is no reason why this policy should not be extended to the production of a large variety of steel products for mining purposes, and it is probable that the installation of further units will to a large extent meet this demand.

With regard to the future outlook of the electric steel industry, there appears to be no immediate sign of any renewed activity in the United Kingdom. Further progress is to be expected in the Colonies, Spain, and South America, and generally in those steel-using countries which were either unable, or had no need, to install steel-making plants during the war. This is to be expected owing to the high price of all European and American steel products, which makes the prospect of local manufacture attractive, and also because manufacturers now have confidence in the electric furnace as a means for converting almost valueless steel scrap into high quality products for the local market.

The technology of the electric process is in practically the same position as a year ago. There has been, however, a growing tendency in this country to improve the quality of electric steel by utilising the deoxidising powers of a true carbide slag to the maximum degree. During the war a great quantity of electric steel was made under conditions of maximum production. This resulted in insufficient deoxidation by slag reaction, and ferro-silicon and other powerful deoxidisers were used, all of which are capable of causing slag inclusions. Now that the full value of carbide slag refining is being better understood and more generally utilised, there is reason to hope that the claims so repeatedly made for the excellence of electric steel will be acknowledged.

In recent furnace design there has been a growing tendency either to eliminate bottom hearth connexions or to arrange the electrical connexions so as to reduce the large proportion of the load current hitherto allowed to pass through the conductive hearth. The application of three-phase current is becoming more general, and in America it is stated that the three-phase design is [illegible] accepted almost as the standard. Further attempts have been made to seal electrodes where they pass through the roof of steel furnaces, and with this object the F.I.A.T. Co. have introduced a special construction.[1] The need for electrode economisers is well recognised as they have the double advantage of reducing electrode consumption and of preventing entry of air into the furnace during the deoxidising stage of the process.

FERRO-ALLOYS.

The ferro-alloy industry has been affected by the present trade depression and cessation of armament manufacture even more than the steel industry. The consumption of ferro-silicon and electrically-produced manganese alloys depends not only upon the output of steel, but also upon the character of the steel produced. It is probable that the requirements of these particular ferro-alloys were greater per ton of steel produced for war purposes than in normal peace times, so that the reasons for the reduced demand are twofold. The demand for ferro-chrome is now very limited, with the exception of the low carbon grades (*i.e.*, 2% and under), which are specially suitable for the manufacture of stainless steel.

In the table below is given the production of various ferro-alloys in Sweden during the war period. It will be noticed that the statistics show a considerable reduction of output in all classes during 1918, which could not alone be accounted for even by a complete cessation of work after the armistice. This reduction of output was no doubt chiefly due to the increased production of ferro-alloys in this and the allied countries.

Swedish Output of Ferro-Alloys (Electric Furnace).

	1914 tons.	1915 tons.	1916 tons.	1917 tons.	1918 tons.
Ferro-silicon	8732	11,819	18,452	19,240	10,705
Silico-manganese iron ..	1304	2328	3196	4367	1305
Ferro-manganese	293	947	1096	1182	2123
Ferro-chrome	1300	242	654	802	258
Ferro-silico-aluminium-manganese	508	785	722	1330	469
Ferro-silico-aluminium ..	64	346	633	1002	354
Ferro-molybdenum	—	—	16	8	—

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[1] E.P. 121,485; *J.*, 1920, 693A.

At the present time many of the Swedish plants are almost idle, and this reflects the general conditions of this industry in other parts of the world.

According to R. M. Keeney[2] there has been a growing demand in America for ferro-molybdenum, which is now being used more largely in the manufacture of complex alloy steels. This alloy is made in single-phase furnaces having a carbon crucible which is connected to one of the electric terminals. In most cases the alloy can be tapped from the furnace by ordinary methods, but the very high grades are made by allowing the alloy to accumulate in the form of a cake, which is later removed when cold. The same authority states that the combined transformer capacity of ferro-alloy furnaces in America amounted to 200,000 k.v.a. at the beginning of the year, but during May it was doubtful whether even 25% of that power was being used.

In England, towards the end of 1918, we were almost independent of foreign sources for our supply of ferro-alloys, although in 1914 the home production of electrically smelted alloys of all kinds was insignificant. Here, again, alloy production has dwindled to a negligible quantity. It is difficult to foresee any material change from the present state of depression, and even supposing the world's steel output approaches a more normal peace-time level, it is unlikely that the demand will meet the combined producing capacity of the world's ferro-alloy centres. The position of the industry at the present time presents almost a repetition of the carbide crisis more than twenty years ago, when other uses had to be found for surplus plant. Although existing plants may continue to suffer, it is probable that further developments in the British Colonies will lead to local production of ferro-alloys, sufficient at all events to satisfy the needs of their own steel works; this expansion would only conform with the general tendency of industrial independence.

There has been no announcement of any real technical advance during the year, but several papers have been read bearing upon modern furnace design, power consumption, and the general metallurgy of ferro-alloy production. C. B. Gibson, R. J. Anderson, and B. D. Saklatwalla contributed papers to the American Electro-Chemical Society in April bearing upon the ferro-alloy industry. According to Gibson, the tendency has been to operate furnaces at the highest load consistent with good mechanical design and desirable electrical conditions, such as low inductance and skin effect. The units used for the manufacture of various ferro-alloys are presented in tabulated form and are of interest. A revival of trade will probably lead to the wider adoption of various refinements to reduce the cost of production, and to this end automatic regulation will no doubt be more generally applied to existing furnaces.

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[2] *Chem. and Met. Eng.*, 1920, **23**, 981.

Other apparatus to keep the combined load of several furnaces below a definite maximum demand figure should also find useful application. This system has already been successfully applied to batteries of steel furnaces for limiting the peak load of power supply stations, and also enables a maximum average load factor to be maintained, which materially reduces the cost of power when purchased on a fixed maximum demand charge.

SYNTHETIC PIG IRON.

The production of synthetic pig iron first received prominence in June, 1914, and since then the process has been widely used in many countries. In places where small steel scrap or turnings are available and where fuel is scarce and at a very high price the process still has possibilities. O. Hasler,[3] while discussing the possibility of establishing an industry for the manufacture of pig iron from scrap and turnings in Switzerland, considers that the process would be unremunerative unless power could be purchased for seven centimes or less. Last year the development of this important process during the war period was reported, and since then there has been a general decline of production. There are, however, plants on the Continent where the process is still being employed.

Apart from the production of pig iron from low-carbon scrap, a further process for refining molten cupola iron is now receiving much attention. The process may be modified according to the actual degree of refinement required. The percentage of phosphorus can be reduced under suitable slag and temperature conditions without any material removal of carbon, and this preliminary treatment may then be followed by further refining under a highly basic reducing slag for the removal of sulphur and adjustment of silicon. The process has been widely developed in the United States for the production of malleable iron castings, and is now receiving close attention in Europe.

ELECTRICALLY SMELTED PIG IRON.

The electric smelting of pig iron in shaft furnaces has continued to engage the attention of numerous investigators and commercial undertakings, and the result of the past year shows steady but slow progress in Sweden, where the process has been worked on a larger scale than elsewhere. In America the economic conditions favour smelting in ordinary blast furnaces, and according to R. M. Keeney[4] the commercial use of the electric process is there being abandoned. There have been numerous and serious technical difficulties to overcome, but these seem to have been so far solved that the process is developing into an important industry in certain countries where economic conditions are favourable. The outstanding advantage of electric smelting is the great saving of fuel, so much so that it is only in localities where fuel is scarce and expensive that electric smelting can compete with the blast furnace. Even then there must also be an abundant supply of cheap hydro-electric power and suitable ores. Some interesting data bearing upon various difficulties met with in furnaces of different types are given in a paper read by E. A. Lof before the Swedish Iron and Steel Institute.[5] Tests were made on Helfenstein and Elektro-Metall furnaces, which enabled various comparisons to be made of their metallurgical and electrical features.

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[3] Schweiz. Elektrotechnische Verein, May, 1919.

[4] *Chem. and Met. Eng.*, 1920, **23**, 980.

It now seems established that the Elektro-Metall furnace can operate with coke in place of charcoal, which marks an advance in the technical development of the process. G. Stig[6] gives data from a run with coke, and points out that, at peace-time figures, a 25% saving in fuel cost is effected by substituting only 50% of coke for charcoal in the furnace charge.

At the beginning of the year there were 13 furnaces operating in Sweden and four under construction, and to this number at least five more have since been added. The Elektro-Metall type appears to be the most popular, and is now constructed in units of 7000 kw. capacity. The chemical composition and physical character of blast furnace iron cannot be exactly imitated in electric shaft furnaces, which produce an iron with a carbon content of about 3–3·2%. For this reason some steel-makers are rather prejudiced against it, as it behaves differently in the open-hearth steel furnaces to the charcoal iron, which contains anything up to 4·5% C. For foundry purposes the electric grey iron is rather harder than blast-furnace iron. Swedish ironmasters, realising the necessity for using the cheapest power available for operating the electric process, are centralising their activities at Porjus, in Lapland. This place is not far from the well-known Galliväre iron ore deposits, and is situated in a forest country and in the vicinity of enormous waterfalls. Favourable contracts for the supply of power have been granted by the Swedish Government, which owns the power plants, and there seems every promise of the process proving a complete success.

At the present time the Swedish pig iron industry is feeling the effect of German competition, and this, added to the general depression in the steel trade, has caused a large number of both electric and blast furnaces to go out of commission. This may be a temporary phase, and when more normal production is possible the electric process will again assume an important share of the industry. Under conditions existing during the first half of 1920, electric pig iron could be produced 15–20% cheaper than a similar grade of blast furnace iron in Sweden, but this was only possible at favourable localities.

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[5] See *Elec. World*, 1920, **75**, 4.

[6] *Chem. and Met. Eng.*, 1920, **23**, 1, 29; *J.*, 1920, 593A.

Apart from the shaft furnaces which have been mentioned above, the pit or open alloy type of furnace has also been used with success. It is doubtful whether the smelting costs are as low as with the Elektro-Metall furnace, which has a high thermal and fuel efficiency due to gas circulation, but on the other hand the fixed charges and outlay of capital are less. The process has been conducted at Trollhättan with this type of furnace, and high silicon grey iron is easily produced.

NON-FERROUS METALS AND ALLOYS.

The development of electric furnaces for melting non-ferrous metals has made further advances during the year, although it must be admitted that the progress has been confined to the United States of America. There are now numerous types in use, based upon various principles of electric heating. A series of articles by H. W. Gillett[7] have been published, in which the author has dealt at considerable length with the development and present status of the industry. The technology of furnace design and the metallurgical functions performed are also fully described. These articles are worthy of careful study by those specially interested in non-ferrous melting. The following types of furnace are now in use in the U.S.A., and are classified in the following table according to the principle of heating adopted. The number actually in operation on June 1, 1920—to quote the same authority—is also given :—

Type of furnace.	Principle of heating.	No. in use.	Total tons capacity per heat
Héroult, Snyder ..	Direct arc	11	7½
Rennerfelt	Indirect arc, stationary ..	7	4½
Detroit	Indirect arc, moving	40	46
Booth	Indirect arc, moving	10	9
American	Indirect arc, moving	1	½
Bailey	Resistance, reflected heat ..	50	41½
General Electric ..	Reflected heat from smothered arcs	4	5½
Ajax-Wyatt	Induction-vertical	93	70½
Hoskins	Induction-horizontal	1	⅛
Bennett	Contact resistance heating ..	7	11
Ajax-Northrup, Baily	Crucibles	7	⅛
		231	196¼

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[7] *Foundry*, 1920, **48**, 177 *seq.*

Recent reports[8] show a further increase in the number of furnaces installed. At the beginning of September the number of furnaces of all kinds installed or contracted for in the United States and Canada had increased to 385, and of the total furnaces employed about 33% are being used for foundry purposes. The Ajax Wyatt induction furnace was credited on September 1st with 176 installations, and it is interesting to note that four of this type are being installed in France. Further increase in the number of Detroit, Booth, and Baily furnaces has also been reported since June 1st. The direct arc furnace is only suitable for melting metals and alloys having a high temperature of volatilisation, such as nickel alloys and bronzes. This also applies to the Rennerfelt fixed type, in which the arc is deflected downwards towards the metal charge. Fixed indirect arc furnaces with horizontal electrodes are also open to the same objection, but to a limited extent, and it was to overcome this difficulty that oscillation or rotation of the furnace was introduced. There are now several types of single-phase furnaces working on this principle, which was first publicly introduced by the United States Bureau of Mines. These furnaces are built in units up to one ton and more, and, owing to the rapid rate of power input obtainable with arc heating, are highly efficient for melting. H. M. St. John[9] has published results of the performance of one-ton Detroit furnaces at various plants, which show a power consumption of 200–300 kw.-h. per ton in an eight or nine hour day. Electrode consumption ranges from 2·4 to 3·5 lb. per ton. The chief feature is the low metal loss when melting red or yellow brass; from figures obtained at various plants using the one-ton unit, the maximum metal loss amounted to 1·02%, while the average was about 0·6%. The average time of each melt was 1–1¼ hrs. These figures indicate the general performance of the indirect arc rocking furnaces. The Baily resistance furnace has also made progress, and is now being introduced in England. Its special advantages are reliability, simplicity of operation, adaptability to all grades of brass, reduced metal loss and labour charges, and elimination of crucibles. The electric load is also very steady and is regulated by a variable voltage switch, which can immediately alter the transformer connexions on the primary windings. The General Electric furnace generates heat over a large area, and has the great advantage that three-phase current can be used. The thermal efficiency is, however, low, owing to the system of indirect heat transference which is adopted to distribute the intense heat from smothered arcs.

It is now undoubtedly accepted that electric melting enables better quality of metal to be produced than from crucibles, and it is largely due to this that the electric furnace is gaining extended application. Little use has so far been found for melting aluminium alloys in foundries by electricity, but according to A. G. Lobley[10] a large resistance furnace is in use at an aluminium factory for melting crude ingots cast from the reduction furnace.

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[8] *Metal. Ind.*, 1920, **18**, 382.

[9] *Foundry*, 1920, **48**, 403; *Metal Ind.*, **18**, 211.

According to various authorities, further progress is expected in America, and there seems every prospect of development in Europe, as soon as the present trade depression is less acute.

There are at present three furnaces of the Héroult type in England, with a total capacity of 4 tons, employed for the manufacture of cupro-nickel, nickel, and other non-ferrous materials not containing zinc.

Zinc Smelting.

The electro-thermal process of zinc smelting has made no further commercial progress during the year. This is primarily due to the universal depression of the zinc industry, which, in England, had reached an acute level towards the end of 1919. Large plants were erected in Norway for smelting complex zinc ores, but these are at present unable to operate owing to the low price of spelter. At the Glomfjord plant in Norway there are twenty furnaces of large capacity being equipped with the latest type of induction voltage regulation. Other plants of smaller capacity are awaiting a favourable time to renew smelting operations. The condensation of the zinc vapour has proved the most difficult problem to solve, and zinc metallurgists in Scandinavia have been concentrating their efforts in this direction. It is now claimed that 65–70% of the reduced zinc can be recovered as crude spelter in one smelting operation, which marks a distinct improvement upon the 50% recovery a few years ago.

Electrolytic Zinc.

Considerable advance has been made in this department of the metallurgy of zinc during the year. About six years ago the problem of electrolytic zinc extraction was taken up by the Anaconda Copper Mining Co. with the object of treating complex concentrates containing only 33–35% Zn. Experimental work was carried on for more than 12 months and exhaustive trials were made on the effect of various impurities in the electrolyte. As a result of this work it was decided to erect a ten-ton plant and this was put into commission in November, 1915. This plant operated successfully, and it was then decided to erect a further plant at Great Falls, capable of producing 100 tons a day. This plant was completed in December, 1916, and further enlarged in 1918.

A full description of the plant and process as now developed and practised at Great Falls, Montana, has been published.[11] One of the secrets of successful operation is to use an electrolyte free from all metals more electro-negative than zinc, such as copper, cadmium, lead, arsenic, antimony, etc. The latter are specially injurious, even when present to the extent of 1 mg. per litre. Traces of impurities in zinc increase its solubility in dilute sulphuric acid as much as fifty times, so that the presence of the above-mentioned metals promotes re-solution of the deposited zinc. Under adverse conditions, hydrogen is evolved at the cathode in place of the deposition of zinc, and for this reason the efficiency of the process, in terms of zinc deposited, is vitally dependent upon the impurities present in the electrolyte. It has also been found that cobalt is a most injurious impurity, fifteen parts per million parts of solution being fatal to electrolysis. Cobalt, however, can be very completely removed by various precipitants.

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[10] *J.*, 1920, 226T.

[11] Amer. Inst. Min. Met., Feb., 1921.

A highly purified zinc solution can be regularly obtained, provided the iron is thoroughly oxidised before its precipitation and sufficient zinc dust is added to satisfy the copper, cadmium, and lead. Arsenic is removed as ferric arsenic and, to complete its precipitation, it is important to ensure thorough oxidation of the iron. This is effected by the oxidised manganese salts in solution, which owe their presence to the manganese in the ore and to its subsequent oxidation in the electrolytic vats.

Aluminium cathodes and sheet lead anodes are now being used. Aluminium, although the best metal to use, is not altogether free from trouble, as it is slowly dissolved by acid above the level of the electrolyte solution. The cost of aluminium due to this amounts to 75 cents per ton of zinc deposited. A small quantity of glue is added to the electrolyte from time to time to improve the density of the zinc deposit, which results in smaller melting losses. At the Great Falls plant, the tank house contains six units, which are operated independently. Each unit consists of 24 rows of cascades, each composed of six cells placed end to end. The cascades are set out in pairs to facilitate removal of cathode plates and each pair is fed from the same supply pipe. The cascades are thus operated in parallel while the cells are in series. The cells are 10 ft. 3 in. long, 2 ft. 10 in. wide by 5 ft. deep. The cathode plates are submerged to a depth of 3 ft. and are spaced about 1¾ in. from the anode plate. The cells of each unit are connected electrically in series, and are served by a rotary converter of 5800 kw., which can deliver about 10,000 amps. at 580 volts. Thus each of the 144 cells operates at a voltage of about 3·8 and the current density at full load is about 30 amps. per sq. ft. The cathodes are stripped every 48 hours and produce two sheets of zinc weighing from 15 to 20 lb. each. They are washed in hot water and surfaced with a wire brush before being returned to the cell room; this latter operation is necessary, otherwise the zinc deposit does not adhere firmly and is then likely to undergo re-solution in the tanks. The zinc cathode sheets go to the melting house without preliminary washing. In designing the vat room, care has to be taken to insulate the floor from the tanks, bar lines, and ground, while rubber shoes are issued to the men as a further safeguard against electric shocks. At the Great Falls plant the finely pulverised zinc concentrates, which contain about 33% Zn and 20% Fe, are roasted at a low temperature and in such a manner that 20% of the zinc content is soluble in water and about 82% soluble in 2% sulphuric acid. The leaching process is conducted in two stages: (i.) a neutral leach, where the calcine is treated with insufficient acid; (ii.) an acid leach, where the treatment of the calcines is continued with the remainder of the acid. The solution for the first leach consists of one-half the requisite quantity of cell acid containing 11½% H_2SO_4 and 2½% Zn and partly spent leach liquor from the acid leach (0·6% H_2SO_4 and 10% Zn). The calcines are treated in several continuous leaching Pachuca vats, a small quantity of pulverised limestone being added to the leach towards the end of the operation. The following results from the neutral leach:—about 75% of the zinc is dissolved; the iron is oxidised and partly precipitated; gelatinous silica is coagulated and rendered granular; arsenic and antimony are completely precipitated; 80% of the copper is precipitated as hydroxide. The discharge from the leaching vats passes to classifiers, which deliver a clear overflow containing a large percentage of the zinc, 20% of the copper, and some cadmium in solution; this liquor goes to the purifying plant, while the settler product is passed to other vats where it undergoes the acid leaching treatment. Here, the residues from the neutral leach are treated with the same quantity of cell acid as is used in the preliminary leaching process. The discharge from the acid leaching vats passes to classifiers where the clear solution containing the remainder of the soluble zinc and copper is separated from the insoluble residues, which are freed from all soluble zinc by washing and filtering. The clear zinc-copper solutions, after treatment with scrap zinc and iron to precipitate the bulk of the copper, are then returned to the neutral leaching vats, and must not contain more than about ½% of free sulphuric acid. The results of the acid treatment are briefly: solution of the remainder of the acid-soluble zinc and copper; final separation of the leached calcine residues from the zinc solutions; part removal of copper and cadmium; solution of sufficient iron to precipitate arsenic and antimony during the neutral leach; and elimination of arsenic and antimony in the residues, only a fraction being redissolved during the acid leach. It will be seen that the solution from this second leaching operation returns to the neutral leaching vats, whence the clear zinc solution passes to the purifying plant for the complete removal of copper and cadmium, together with any arsenic and antimony that may have escaped precipitation in the neutral leaching vats. These solutions are agitated with zinc dust in stages until all the copper and cadmium is precipitated. The leach from this operation goes to settling vats, and is further clarified by filter presses before passing through storage vats to the electrolytic cells. The sludge, consisting of the copper, cadmium, and zinc, is treated with acid until the copper begins to show signs of solution, which is an indication of the complete solution of the cadmium and zinc. The unattacked copper is collected as a rich slime, while the cadmium in solution is again precipitated by zinc dust, and is separated as a slime containing 12% Cd.

The Great Falls plant has been operated with great success, and in December, 1918, was capable of producing 150 tons a day. The electrolytic process has a distinct advantage over the electro-thermal since it can produce 10-12 lb. of metal per kw.-day as against 4 lb. under the best electro-thermic practice. The energy consumption is also independent of the zinc values in the concentrates, whereas the electro-thermal process demands a higher energy consumption as the proportion of gangue rises; this follows from the fact that the gangue has to be fluxed and melted.

About three years ago the Judge Mining and Smelting Co., Utah,[12] erected a plant for the treatment of their concentrates, 30 tons being handled daily. The process is very similar to the one worked out at Anaconda, and later operated at the Great Falls lant. The concentrates, containing 35% Zn, 8% Fe, 5% SiO_2, 1% S, 3·5% Pb, and small quantities of copper and cadmium, ndergo only one leaching operation, in which the zinc oxide is issolved together with part of the cadmium and copper. The nsoluble matter is sent to the smelting plant, while the liquor is assed to a tank in which it is agitated with zinc dust to remove all races of copper and cadmium. The purified solution is then umped to storage vats and is ready for electrolysis. The arrange-ent of the cells, size of plates, current density, and voltage are all ubstantially the same as at Great Falls and need no further escription.

The electrolytic process is now being further developed in asmania, where hydro-electric power can be purchased at 40s. er horse-power year. The plant at Risdon, near Hobart, is at resent capable of producing 6000 tons annually of high-grade inc of 99·95% purity, but provision is being made to increase this roduction. The output of this plant, after local requirements are et, has been purchased by the Government for the next nine years t a figure exceeding the market price of prime Western spelter.

The plant of the Consolidated Mining and Smelting Co., Ltd.,

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[12] *Min. and Sci. Press*, 1920, **120**, 409; *Chem. and Met. Eng.*, 1920, **22**, 537.

Trail, B.C., has been also recently described by L. W. Chapman.[13] It is interesting to note that this plant was the first of its type, having been started in 1914; the production now amounts to 75 tons of zinc per day. The calcined concentrates contain 27·0% Zn, 11·1% Pb, 25·8% Fe, 0·03% Cu, 1·8% CuO, 0·9% Mn, and 2 oz. Ag per ton. A double leaching operation is used, as at Great Falls, and the process is almost identical throughout. At the present time the electrolytic product is being sold at a reasonable profit, which is significant in view of the failure of the retort process to operate at the present market price of spelter.

The future of the electrolytic process seems uncertain in countries where the retort process can be conducted under favourable conditions, such as low cost of fuel, fireclay, and other materials.

In 1918 the output of electrolytic zinc in the United States[14] was 38,916 tons, but in 1919 had fallen to about 27,000 tons, equivalent to a reduction of 30·8%; during the same period the output of retort zinc was reduced only by 11%. In November, 1919, all the electrolytic plants had ceased operation, excepting the small experimental plant of the Illinois Zinc Co.

CARBON ELECTRODES.

Certain advances have been made in the manufacture of amorphous carbon and graphite electrodes for use both in furnaces and electrolytic cells.

The development of iron-smelting furnaces and the increased capacity of steel furnaces has created a growing demand for electrodes of large diameter. A diameter of 24 inches was, until recently, the maximum, but now pressed electrodes of 30 in. diameter are being regularly manufactured. The direct pressing method of forming amorphous electrodes is being more widely adopted[15] and is being successfully applied for electrodes of the largest dimensions.

Further data concerning the Söderberg continuous electrode process have recently been published by J. W. Richards,[16] and throw more light upon this comparatively recent innovation. Briefly, the electrode is constructed by filling sheet steel casings with rammed carbon paste. The electrode is lengthened by merely welding on a further section of casing, which is again nearly filled with carbon paste. In practice the electrode is firmly gripped by water-cooled holders, which are suspended in the usual way from overhead crane gantries. The upper end of the built-up electrode passes through the floor of a small chamber in which the lengthening

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[13] *Chem. and Met. Eng.*, 1920, **23**, 227.

[14] *Metal Ind.*, **16**, 455.

[15] *Iron Age*, 1920, **105**, 188.

[16] *Trans. Amer. Electrochem. Soc.*, 1920 (*advance paper*); *J.*, 1920, 119A.

process can be conducted without any discomfort from either gas or heat rising upwards from the furnace. The carbon paste remains in a soft and unbaked condition above a point about halfway up the holder clamps, which are at least 20 in. long. By this process the heat normally conducted away from the furnace by the electrode is used to bake the paste. The casings are constructed of several longitudinal sheet steel segments, rivetted together, and previously bent almost at right angles along one edge so as to form a number of inwardly projecting ribs. These ribs are afterwards cut transversely and then bent alternately to the right and left hand; in this way a large number of short fins are provided, which are intended to reinforce the carbon paste while still in the unbaked condition, and further to provide a large area of contact between the sheet metal and the carbon core.

The filling process is very simply carried out by means of a pneumatic ramming iron, which is suspended above the empty casing and counterbalanced so that the operator has only to guide the stamping head over the paste. This method of making the continuous electrode certainly eliminates the use of costly plant for pressing and baking, and up to this point must be considerably cheaper than pressed electrodes. The sheet casing introduces additional cost in the manufacture of electrodes both in labour and material, but for large electrodes this cost for every ton of carbon paste is very small and quite insufficient to offset the saving effected by elimination of hydraulic pressing and baking. In actual cost per ton of electrodes there is no doubt an advantage in favour of Söderberg electrodes, when not of too small diameter. In spite of reduced cost the continuous electrode could not compete unless it enabled furnace manipulation and metallurgical operation to be conducted with at least the same degree of ease as with the ordinary type. Experience during the past eighteen months shows that the operation of alloy furnaces is actually improved, while all the troubles incidental to electrode breakages are entirely absent. The electrode is lowered through the holder without reducing the furnace load, and delays due to changing or joining electrodes are avoided. This improves the load factor, and consequently the output, which is further benefited by the smooth and uniform condition of smelting. The first trial in America was made at Anniston, Alabama, where an 1800 kw. three-phase furnace was equipped with three electrodes, 31½ in. diameter. The furnace was smelting Caucasian manganese ore, low both in iron and slag-making material. Iron turnings were therefore added, and a portion of the slag from each tap was returned to the furnace for making the proper quantity of slag. According to Richards, the Söderberg electrodes have resulted in smoother running of the furnace, and considerable saving in electrode costs. The reduced consumption is due to freedom from breakages, the elimination of stub and losses and absence of the surface combustion, which sooner or later occurs in the case of pressed electrodes between the furnace charge and the holder; with the Söderberg electrode the holder always grips the electrode at a point not exceeding 12 in. above the charge.

The Söderberg electrode was developed in Norway, and at one experimental plant an electrode 33 in. in diameter, it is stated, has been in continuous operation for 18 months without breaking, or causing any delay to the furnace operation. The process is certainly one with possibilities, and its application on a wider scale may be expected on the resumption of normal trade conditions.

During the year the manufacture of artificial graphite electrodes in England has been successfully established, and all sizes from 12 in. diameter to small welding electrodes are now being produced. This marks a notable advance, and completes the independence of the electro-metallurgical industries at home. Graphite electrodes are also being manufactured in small quantities in Norway and Sweden.

HYDRO-ELECTRIC DEVELOPMENT.

Notwithstanding the present depression of the electro-metallurgical industries, there have been certain notable developments of hydro-electric power schemes in different parts of the world. This development has proceeded rather more in countries where electric power has not previously been used extensively for metallurgical and chemical purposes. Thus, there has been marked activity in the Commonwealth of Australia, New Zealand, India, and other parts of the Empire.

The Government of New Zealand is strongly encouraging the development of hydro-electric power, and has made provision for issuing a loan up to £10,000,000 for the completion of a large system in North Island. The ascertained resources of the country exceed 7,000,000 kw., and the sole right of developing this power is vested in the Government. The reduced output of coal and constant labour troubles are factors which have weighed heavily in the decision to promote this undertaking.

Similar activity may be recorded in Tasm
is being developed for the Electroly ide by the Taylor process
Rolleston a similar plant is being de s, but in spite of its increasing
Rosebury Co. with power for the pr l silk, and similar industries,
zinc per day. come properly established in
In France an enormous project is tion is being erected to work
which entails the canalisation of ng carbon and sulphur in a
scheme twenty hydro-electric station ricity.
715,000 h.p., which represents a large

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[17] *Electrician*, 1920, **84**, 539.

now developed in France. The undertaking is to be completed within 15 years.

In Sweden there are at present immature schemes for the further development of power in the northern districts, which should enable much cheaper power to be purchased in the central steelmaking districts where only an inadequate quantity of hydro-electric power is now being developed.

In England the Severn Barrage scheme is at present attracting great attention, and should it eventually materialise and justify the expectation of the promoters, it will doubtless revolutionise the electro-chemical industries which are now so poorly represented. Parliament is also to consider a scheme for the development of hydro-electric power in Scotland, in which no less than five lochs are to be utilised. There is no doubt that lack of cheap electrical energy is crippling the electro-metallurgical and chemical industries of this country, and it is to be hoped that every encouragement will be given to any sound water-power scheme.

NITROGEN FIXATION.

A modification of the arc process for the fixation of atmospheric nitrogen has been developed, which utilises the principle of the silent electric discharge.[18] The chief advantage claimed is that the gases do not become appreciably heated on passage through the arc zone. Ozone and the oxides of nitrogen are produced by the electrostatic brush discharge, the lower oxides of nitrogen being further oxidised by the ozone and then absorbed in water to give nitric acid. The gases on leaving the apparatus pass on to an absorber containing sodium hydroxide, and then through a Cottrell precipitator. The highest yield of nitric acid so far obtained is 9·8 g. per kw.-h, but this may be improved upon by using better absorption apparatus.

The original arc process, which is operated by the Norsk Hydro-Elektrisk Kvaelstofaktieselskab at Notodden and Rjukan, continues to prosper in spite of the more modern synthetic and cyanamide processes of fixation. The latter process has undoubtedly received
[illegible] since it has been found difficult to apply the crude
output, which is [illegible] the success of this process depended
condition of smelting. The the product as a fertiliser, and, failing
Anniston, Alabama, where a compete with the synthetic process
equipped with three electrodes ia. The position of the cyanamide
smelting Caucasian manganese certain and at the present time a
material. Iron turnings were t are shut down. The Norwegian
slag from each tap was return large quantity of ammonia which has
quantity of slag. According pt during the war, and it is probable
have resulted in smoother ru
saving in electrode costs. cEachron, *Trans. Amer. Electrochem. Soc.*,

that requirements from this source may open up a renewed demand for Scandinavian ammonia produced from cyanamide.

During the year, the final report of the Nitrogen Products Committee was published,[19] and this report constitutes a most complete treatise on the subject, both from technical and economic standpoints. The construction of a large works for the manufacture of synthetic ammonia and derivatives was commenced by the British Government, before the armistice, at Billingham, on the North-East coast, and the work is now being continued by private enterprise.

ALKALI AND CHLORINE.

There are now several excellent cells in use for the production of caustic soda and chlorine from brine solutions. They were largely used in America during the war for the generation of chlorine gas, but were not so widely adopted in Europe. France, at the beginning of the war, had only a few works preparing chlorine by purely chemical methods, and only two which employed an electrolytic cell.[20] When a vastly increased output became imperative, the Outhenin-Chalandre cell was at first chosen, not because it had any particular advantages over the American cells, but because it was better known and could be more quickly adopted. La Société pour l'Industrie Chimique at Bâle used another type of cell with an asbestos diaphragm but owing to the general construction there is risk of caustic soda diffusing towards the anode and there combining with chlorine to form chlorates or hypochlorites; this cell was responsible for half the output of chlorine in 1918. The Solvay cell has also been used, but, owing to various inherent objections, is not so satisfactory as more modern types. The Allen-Moore and Nelson cells, which were used so extensively in America, are now being introduced into France, and may eventually supplant the French cells above-mentioned. A large plant was recently erected in Norway to operate the Nelson cell, but according to the latest reports, it has not yet started production.

There has been no recent advance in the technology of this subject, the various modern cells having all been amply described in former years.

MISCELLANEOUS PROCESSES.

The manufacture of carbon bisulphide by the Taylor process has been continued in the United States, but in spite of its increasing demands as a solvent in rubber, artificial silk, and similar industries, this process of manufacture has not become properly established in Europe. In France, a small installation is being erected to work this process, which consists of combining carbon and sulphur in a bed of coke heated by resistance to electricity.

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[19] See *J.*, 1920, 25R.

[20] *Rev. Prod. Chim.*, 1919, **22**, 501.

Experiments are being made in Scandinavia to manufacture pure phosphoric anhydride and to produce ferro-phosphorus as a by-product by the reduction of low grade ferruginous phosphate rock with carbon in an electric furnace of the shaft type. Air is admitted in the upper part of the furnace and oxidises the phosphorus vapour to phosphoric anhydride, which is subsequently condensed.

Regarding the manufacture of calcium carbide, there is nothing much to report. The industry has largely suffered owing to the reduced demand for calcium carbide, and to the unsatisfactory progress of the cyanamide process for the fixation of atmospheric nitrogen. In Scandinavia numerous plants have been either idle or operating under greatly restricted output. In conformity with the general development of electro-chemical industries within the British Empire, it is interesting to note that a 3000 kw. plant has been successfully established in Tasmania.

OILS, FATS, AND WAXES.

By JOHN ALLAN,

Messrs. Joseph Crosfield & Sons, Ltd., Warrington.

THERE is little doubt that during the past year those engaged in industries concerned with the preparation and use of oils and fats have found their minds more fully occupied with economic considerations than with published matter pertaining to the technical or scientific side of their business.

During, and immediately subsequent to the war period, and largely because of the nation's food needs, industries directly or indirectly concerned in the manufacture of fatty foods were so developed that, besides handling a much greater bulk of materials, the produce of these plants is much more varied in its kind. Probably, no better example of this growth is to be found than the fact that the total capacity of the pre-war British margarine plants was 2500 tons per week, whereas the home capacity to-day is estimated to be about 10,000 tons, and the consumption about 8000 tons per week. It is clear that to meet the demand for the edible fats required by such an increase in margarine manufacture a corresponding increase in crushing and refining and deodorising plants must have taken place, and it can be said definitely that, so far as capacity is concerned, this country is fully equipped to supply its own requirements of edible vegetable fats. It cannot be assumed that we shall retain this home market without a struggle, since the world's supplies of oleiferous nuts and seeds are now open to Continental manufacturers, and competition is already arising from the extensive plants in France, Holland, and Germany, which were deprived of raw materials during the war period. The development of this position will naturally be watched with keen interest.

It has been stated frequently of late that the world's demand for oils and fats is now equal to, if not already in excess of, possible supplies, and the recent determination to reduce the area of planted cotton in Egypt by 30%, coupled with an agitation for a similar and even greater curtailment in the United States, cannot be viewed without concern since cotton-seed oil is of prime importance as a foodstuff, both as to quality and quantity, and any shortage in the supply of seed would be little short of a disaster under existing conditions. It is true that a permanent shortage of cottonseed oil could be made good by increased plantings of arachis and sesamé, but the fact that the cotton plant yields both fibre and seed will always give it a commanding position in any competition with plants cultivated for oil-seeds alone.

It has already been pointed out in these reports that published investigations of new sources of fats and oils are frequently lacking in such all-important information as the available supplies and cost of delivery at a crushing mill. Much of this arises from a lack of appreciation of the large quantities required to make handling in a modern mill an economical process, and that a plant or tree bearing an oleiferous seed may be of quite frequent occurrence without making it possible to use its seeds economically as a source of oil. Nevertheless certain, as yet, little used oils must become of considerable importance in the near future. The Report of the Agricultural Department of the Malay States for 1919[1] contains a reference to the investigation of rubber-seed which is being carried out with the view of obtaining the useful drying oil which is contained in the seeds of the Para rubber tree (*Hevea Braziliensis*). It is pointed out that the seed on storage deteriorates and yields an oil containing a high percentage of free fatty acids (up to 25%), whilst freshly collected seed gives an oil with a very low acid content. No indication is given of the reason for this rapid depreciation, but it is undoubtedly to be attributed to the fact that the seed contains a highly active lipase comparable with that of castor seed. The action of this enzyme is greatly facilitated by the fact that the peculiarly soft kernel of the seed is contained in a thin, brittle shell which is easily broken during storage and the enzyme is thereby brought into contact with the released constituents of the oil cells. For this reason it would appear that the preparation of rubber-seed oil must be a local industry at or near the place of origin of the seeds.

Cohune nuts.—Up to the present only slow progress has been made in developing the large palm-bearing districts which are situated in and about the South American countries bordering on the Gulf of Mexico. It is reported[2] that the annual crop of cohune nuts in British Honduras alone amounts to 50,000 tons, of which only about one quarter can be used commercially owing to transport and labour difficulties, but when it is considered that this palm is common in Nicaragua, Costa Rica, and elsewhere and that it is only one of a number of similar palms, the possibilities of development are at once seen to be great. It is a characteristic of these palm nuts that the thick, hard shell forms a very large proportion of their weight (the kernel is usually about one-seventh of the whole weight of the nut) so that transport and labour charges will be greatly reduced when a portable cracking machine of high efficiency has been invented. The machines at present in use cannot be said to meet all requirements.

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[1] *J.*, 1920, 381R

[2] *J.*, 1920, 115R.

Castor oil.—The special applications of castor oil during the war years having largely ceased, the demand for this oil is in no way so great as formerly. Nevertheless, the results of the cultivation experiments in New South Wales[3] are not without interest from an economic point of view, particularly to Australian users. The fact that the oil-free residue of the seeds has only a manurial value means that the oil must bear a larger proportion than usual of the manufacturing costs and, therefore, any saving in transport charges that can be effected is of special importance in this case. Seeds from two naturalised forms and four cultivated varieties of the castor plant grown in New South Wales were found to contain the normal average of 50% of an oil which was of quite satisfactory quality. Experiments on a much larger scale are in contemplation.

Maize oil.—A recent United States Government publication[4] dealing with the preparation and uses of this oil states that the output in 1918 from some 20 factories producing this oil amounted to the very considerable quantity of about 50,000 tons, of which about 34,000 tons was refined for edible purposes. No figures are available for 1919. It may be assumed, however, that since the oil is not specially suitable for margarine production it will not occupy any preferential position amongst the oils ordinarily used for this purpose, although it is estimated at present that about 75% of the oil produced is being used for edible purposes. One of the principal technical uses for which it has been in good demand is the preparation of rubber substitutes, for which purpose both crude and refined oils are employed.

Coconut oil.—The New York Intelligence Office of the Netherland-India Government has recently supplied information[5] which indicates the extent to which the vegetable oil industry in the Dutch East Indies has grown during the last few years. This is specially marked in the case of coconut oil, which is now produced in large hydraulic crushing plants situated chiefly in Java, where some of the mills are stated to have an output of 2000 tons of crude oil per month. According to the Government figures the annual output at the end of 1920 from these Colonies will approximate to about 400,000 tons, which figure includes the production of small primitive mills operated by natives and estimated to be about 25% of the whole. The United States is the largest user of the copra and oil produced in these islands, the total import being second only to that obtained from the Philippine Islands.

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[3] *J.*, 1920, 111R.

[4] *U.S. Dept. Agric.*, *Bull.* 904, Oct. 29, 1920.

[5] *Cotton Oil Press*, 4, No. 4, Aug., 1920.

Palm oil.—This oil is becoming a leading commodity of the eastern coast of Sumatra, where large plantations are now being established, because initial experiences have resulted in larger profits than from the cultivation of the coconut, and since any fall in the price of edible fats would affect copra as well as palm kernels and palm oil it seems preferable to open up plantations of oil palms, where conditions are suitable, than to extend coconut estates.

As a result of the work carried out in West African agricultural stations and the experience gained in Malaya and Sumatra, it is now clear that cultivated palms produce a much larger yield of fruits than the wild trees of West Africa. The plantation industry is at present in its infancy, and practical experience on a commercial scale is almost wanting. Present-day knowledge and an able discussion of future prospects are contained in a recent publication of the Imperial Institute.[6]

Extensive cultivation experiments are now being carried out by the Dutch Government authorities, both in Sumatra and in Java, and the results of their work should go far to provide the information which is required if plantation work is to be carried out on scientific lines. Very little is known as to the yield of fruit and ultimately of oil and kernels from the different varieties of the oil palm, and it is not easy, therefore, to select any particular variety for cultivation. Experience has shown hitherto that it takes several generations to obtain a race of palms bearing fruits containing thin-shelled nuts true to type. In the Gold Coast, seedlings of the "Abobo-be," a recognised thin-shelled variety, gave both hard- and soft-shelled nuts in the same bunch, and in the Cameroons, where the "Lisombe" variety was planted, only a small proportion of the seedlings came true to type in the first generation. It seems doubtful whether the elaborate procedure of selection over an extended number of years is necessary in view of the results already obtained in Sumatra.

GENERAL CHEMISTRY.

It is still necessary to remark on the small amount of new work dealing with the general chemistry of oils and fats published during the year. This may be accounted for by the many difficulties which surround such investigations, but it is to be noted, with approval, that there is a distinct tendency to investigate more fully the composition and properties of individual constituents of oils and fats rather than the more or less variable complexes which constitute the commercial articles.

The preparation of fatty acids by the oxidation of hydrocarbons of petroleum and similar origin presents many attractions from an economic point of view. The utilisation of atmospheric oxygen for this purpose, with and without the aid of catalytic agents, has been the basis of many investigations, and this line of research is still being pursued.

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[6] *Bull. Imp. Inst.*, 1920, **18**, 209-252.

L. Ubbelohde and S. Eisenstein,[7] by heating purified paraffin wax for 12 hours with 1% of manganese stearate and 2½% of water at temperatures below 200° C., obtained a mixture of fatty acids containing 18–20% of unsaponifiable matter. The fatty acids, which had a saponification value of 200, contained butyric, valeric, and probably caprylic acids, but no known solid fatty acids could be identified.

F. Fischer and W. Schneider,[8] following somewhat on the lines of the old and well-known patent of Schaal,[9] have endeavoured to oxidise paraffin wax by means of compressed air in presence of an alkali and have obtained a yield of fatty acids as high as 90% of the paraffin used. The rate of oxidation varies with the temperature and is proportional to the pressure of the air. Using sodium carbonate solution at about 170° C., iron, manganese, and copper have approximately equal catalytic effects. The fatty acids are true monobasic fatty acids containing an uneven number of carbon atoms. The following have been definitely identified: $C_{19}H_{38}O_2$, m.p. 65°–66° C.; $C_{17}H_{34}O_2$, m.p. 58°–59°; $C_{15}H_{30}O_2$, m.p. 50°–51°; $C_{13}H_{26}O_2$, m.p. 38° C. If the oxidation of paraffin by blowing air through it at 135°–145° C. be carried out in the absence of water, acid anhydrides and not fatty acids are produced. The anhydrides can be separated from unaltered paraffin by means of acetone.

K. Löffl,[10] who contradicts the statements of Schaal[9] and Franck[11] as to the action of alkalis as oxidation catalysts, states that the best results are obtained by oxidising at 115°–120° C. under a pressure of 3 atm. and with agitation for about 7 hrs., using as a catalyst a lead or mercuric compound in the presence of water which is an essential factor. The product of this treatment is a mixture of very variable composition which contains water, fatty acids, aliphatic aldehydes and ketones, and unsaponifiable matter.

C. Kelber[12] has obtained, by the action of oxygen on paraffin wax, a residue amounting to 90–100% of the original substance. This residue is stated to contain capric, myristic, palmitic, heptadecoic, stearic, and arachidic acids, and also an acid isomeric with palmitic acid, possibly identical with Bergmann's isopalmitic acid.

A. Grün,[13] as the result of an extended investigation, is of the opinion that many statements as to the efficiency of so-called

[7] *Chem. Zentr.*, 1920, **91**, II., 22; *J.*, 1920, 495A.

[8] *Ber.*, 1920, **53**, 922; *J.*, 1920, 521A.

[9] *J.*, 1885, 679.

[10] *Chem.-Zeit.*, 1920, **44**, 561; *J.*, 1920, 604A.

[11] *Chem.-Zeit.*, 1920, **44**, 309; *J.*, 1920, 395A.

[12] *Ber.*, 1920, **53**, 1567; *J.*, 1920, 714A.

[13] *Ber.*, 1920, **53**, 987; *J.*, 1920, 521A.

oxidising catalysts are erroneous. He further states that the nature of the products of reaction is determined by the conditions under which the oxidation is carried out and that the whole series of acids from those of high molecular weight down even to formic acid may be produced. Hydroxy-fatty acids, unsaturated acids, the higher alcohols, and some aldehydic and ketonic substances are also formed.

It cannot be said that the work in this field, as yet, presents any very definite conclusions, and much that has been published is markedly contradictory. Considering the complex nature of the product of oxidation and the difficulties which surround a satisfactory identification of its constituents many of the statements as to the nature of the acidic substances present must be accepted with considerable reserve.

The great increase in the drying power which is conferred upon an oil by subjecting it to the process of boiling, and which is invariably accompanied by what is called polymerisation, has not yet been satisfactorily explained. A valuable contribution to the theory of the changes which take place during polymerisation is due to A. H. Salway,[14] who puts forward the view that at the high temperature employed there is first a liberation of one or more fatty acid radicles which then condense with the unsaturated linkages of the fatty oil. This condensation takes place between the free acidic groups on the one hand and the unsaturated linkages of the fat on the other hand, resulting in a partial saturation of the fat and the setting free of one hydroxyl group. At the high temperature required for polymerisation, however, such a compound might be expected to condense with the formation of a polyglycerol derivative, thus accounting for the increased density of a polymerised oil. The two main reactions which occur are therefore:—

(*a*) The union of a carboxylic group of a fatty acid with an unsaturated linkage or series of these, and

(*b*) The condensation of a so-called diglyceride with the formation of a polyglyceride.

Experimental evidence of (*a*) is forthcoming from the fact that if the fatty acids from linseed oil and palm oil be heated separately at 270° C. for six hours in the presence of carbon dioxide, in the case of the linseed oil fatty acids a reduction in iodine value is accompanied by a reduction in acid value, whilst with the comparatively saturated acids of palm oil there is no appreciable reduction either in iodine value or in acid value. Since fatty acids behave thus it is only reasonable to conclude that a similar reaction would occur between a fatty acid and an unsaturated glyceride. It has been proved that if a quantity of fatty acid be added to an almost neutral oil and the mixture subjected to a polymerising temperature the fall in iodine value is accelerated, and further that if the fatty acid be replaced by glycerol the fall is retarded.

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[14] *J.*, 1920, 324T.

Proof of the second stage of the theory involving a condensation of the glycerol radicle is not so readily forthcoming, but in view of the fact that monoglycerides when heated to high temperatures readily undergo changes with elimination of water there is considerable evidence to support the deduction.

The properties of the products obtained by the action of nitric acid upon fatty oils and resins have frequently been claimed to have wide technical applications, but though much has been published, chiefly in patent literature, concerning them, little is known of the chemical composition of the products of nitration.

L. G. Radcliffe and C. Polychronis[15] have made a valuable contribution to our knowledge of the nitration reactions and of the nature of the products, particularly as their work has been carried out on individual fatty acids as well as upon the mixtures which occur in natural oils. The action of nitric acid upon oils varies with the nature of the fatty acids which they contain, and also with the temperature at which the reaction is carried out. Saturated fatty acids, such as stearic acid, are very little acted upon in the cold, either by strong nitric acid or by fuming 99% acid, but are oxidised by hot nitric acid, with the formation of isonitrostearic acid and other compounds. Unsaturated acids, such as oleic acid, are slowly acted upon by cold strong nitric acid, but when treated with fuming nitric acid, even at a low temperature, they yield nitrated products, water being simultaneously formed probably by the nitration of the hydroxyl group produced by the action of nitric acid on the double linkage. Nitration of such acids as oleic acid almost eliminates the iodine value and the nitrated product has a distinct hydroxyl value, and it is found that the products of saponification are never entirely free from nitrogen. It is probable that the nitrated products consist of several substances containing NO_2 and NO_3 groups. It would appear that the glycerides of unsaturated acids form corresponding compounds under similar treatment.

Ricinoleic acid and castor oil behave towards nitric acid as do oleic acid and olein, but the action of nitric acid is apparently facilitated by prior sulphonation. If sulphuric acid be mixed with nitric acid and the mixture used as in ordinary nitration processes, the action proceeds at a much lower temperature, but the product contains no more nitrogen and is always much darker in colour.

MARINE ANIMAL OILS.

M. Tsujimoto has continued his interesting work on shark liver oils[16] and has found that although the hydrocarbon squalene is of most frequent occurrence in the liver oils of the *Squalidæ*, it is also found in the liver oils of several other species as, for instance, the *Cetorhinidæ*, it having been detected in the oil obtained from the frill and basking sharks. It would appear that the hydrocarbon is of wider occurrence than at first was thought, since it has been proved to occur in the egg oil of the Japanese and frill sharks.[17] Tsujimoto considers that although Chapman's "spinacine"[18] isolated from Portuguese shark liver oils differs slightly from "squalene" in some of its physical characters, the two hydrocarbons are probably identical.

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[15] *J. Soc. Dyers and Col.*, 1920, **36**, 65; *J.*, 1920, 305A.

[16] *J. Ind. Eng. Chem.*, 1920, **12**, 63; *J.*, 1920, 197A.

It is doubtless owing to the recent high prices for linseed oil that a considerable amount of attention of late has been given to the possibility of using as a paint-vehicle, oils obtained from certain fish of common occurence along the American coasts, chiefly by H. A. Gardner and his co-workers. It is obvious that the price of linseed oil will largely determine the possibility of using such oils economically.

Yellow tail fish oil,[19] obtained from *Seriola dorsalis*, which is abundant on the Southern and Lower Californian coast, is a light-coloured oil having iodine value 177–180. Exposed to air, on glass, it dries to a fairly firm film in 105 hours as compared with 95 hours for raw linseed oil. When mixed with 10% of lead and manganese linoleate drier it dries in 15 hours as compared with 12 hours for linseed oil similarly prepared.

H. A. Gardner has also examined oils obtained from the king and silver salmon[20] which were found to have, respectively, the following characteristics: Sp. gr. 0·9268 and 0·9183; $n_D^{25}=1·4788$ and 1·4753; saponification value 183 and 193·3; iodine value 159 and 150·6. Raw oil from the king salmon was tacky after 3 days' exposure, but with 10% drier gave a fairly firm film. Silver salmon oil when mixed with a suitable drier dries well in 18 hours, especially when blown.

Channel catfish oil,[21] also examined by H. A. Gardner, had the following characteristics: Sp. gr. 0·9234; $n_D^{25}=1·4741$; acid value, 10·9; saponification value 192; iodine value 123. It is unsuitable for paints or varnishes in the raw state, but dries better after heat treatment. None of the above oils can be considered as being more than an indifferent substitute for linseed oil in paints, though they might be used in small proportions in admixture with it.

Whale oil as ordinarily found on the market is a mixture of the oils obtained from the blubber and flesh of various *Balænæ*, and some of these are reputed to give a better quality of oil than others. Few analyses of authentic specimens of oil from a particular variety of whale have been published so that the characteristics of a sample of oil from the dike or finner whale, *Balaenoptera borealis,* given by S. Ueno,[22] are of interest: Sp. gr. at 15° 4° C., 0·9224; acid value 0·24; saponification value 185·2; iodine value 144·2; acetyl value 3·2; Hehner value 96·0; $n_D^{20} = 1·4754$; unsaponifiable 0·7%. The oil when hydrogenated until the iodine value was 3 had m.p. 58° C. Except for the fact that the iodine value is somewhat higher than the average it is difficult to see how this product of one of the less highly esteemed whales differs from good average oil.

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[17] *J. Ind. Eng. Chem.*, 1920, **12**, 73; *J.*, 1920, 197A.

[18] *J.*, 1917, 392, 602.

[19] *Paint Manufrs. Assoc. U.S.*, *Circ.* 86, 1920; *J.*, 1920, 304A.

[20] *Ibid.*, *Circ.* 92; *J.*, 1920, 494A.

[21] *Ibid.*, *Circ.* 92; *J.*, 1920, 495A.

The decision given in a law action heard in the Appellate Division of the Supreme Court of South Africa [23] as to the quality of the lower grades (Nos. 3 and 4) of whale oil has clearly stated that such oils must be obtained from whales of the genus *Balaena,* and must not contain any oil obtained from whales which furnish sperm oil, as has sometimes been found to be the case. The following is an abstract from the judgment as delivered by Sir James Rose-Innes, Chief Justice: "It is clear from the evidence that oil derived from whales falls into two different categories. That yielded by the various species of the genus *Balaena* (such as the right or humpback whale) is in one. That yielded by the sperm whale (Cachelot) and the Arctic sperm whale is in another. . . . Under these circumstances I am forced to the conclusion that No. 3 Whale Oil denotes, for trade purposes, the third grade of oil obtained from whales other than sperm whales."

M. Tsujimoto [24] states that the highly unsaturated fatty acids occurring in marine animal oils may be separated easily by taking advantage of the fact that the lithium salts of these acids are readily soluble in acetone containing 5% of water whereas the salts of the saturated and less unsaturated acids are either insoluble or only slightly so. The amounts of highly unsaturated acids in fish oils determined by this method are higher than those calculated from the yields of the fatty acid polybromides. As a result of his investigation of the unsaturated acids obtained from Japanese sardine oil he suggests that the oil contains a highly unsaturated fatty acid of the composition $C_{20}H_{30}O_2$. It is within the present writer's knowledge that such an acid is to be found in several oils of marine origin, including whale oil.

DRYING OILS.

Our knowledge of the reactions which take place during the drying of linseed and similar oils and the effect of varying atmospheric conditions upon these reactions is very slight, but recent work is bringing us nearer to an explanation of many points hitherto little understood. A. de Waele,[25] by the observation of films of oil distributed on paper and exposed to air under varied conditions, concludes that the presence and nature of the drier does not affect the value of the periodic variation in weight after the first inductive period. It would appear also that since water is a product of the reactions accompanying drying, an equilibrium condition can exist and that moisture in the atmosphere inhibits oxidation in proportion to its amount, and especially so when the oxidation is proceeding in the light. The variations in the curves representing drying in the dark seem to be more dependent upon relative humidity than on the pressure of water vapour. It is further considered that oils which have dried rapidly under the influence of lead or lead-manganese driers do not ultimately show such a rapid decomposition as the less rapidly oxidised oils which contain either no driers or manganese alone.

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[22] *J. Chem. Ind., Tokyo,* 1920, **23**, 1028; *J.*, 1920, 825A.

[23] *J.*, 1920, 279R.

[24] *J. Chem. Ind., Tokyo,* 1920, **23**, 1007; *J.*, 1920, 825A.

The great attention which has been given of late to the mechanism of catalytic reactions has given rise to many theories as to the *rôle* of siccatives in the drying of oils. R. S. Morrell[26] has collected these various theories, and from a full discussion of his own work and that of others he concludes that the chemical properties of the metals used as driers will not account for their behaviour and that more attention must be paid to the study of the catalytic oxidation of oils from the conditions at the interfacial surface, whereby connexion may be established between the superficial forces and those manifested in the chemical changes which are known to occur during oxidation.

Much attention has of late been given to the possibility of using the lumbang oils, products of various *Aleurites* which are common in the further East, as substitutes for linseed oil. H. A. Gardner[27] is of opinion that these oils, possessing as they do marked drying qualities, should be classed rather with tung oil than linseed oil. Soft lumbang oil obtained from the seeds of *A. trisperma* dries on glass with the opaque crystalline appearance characteristic of tung oil; but a perfectly clear film is obtained when the oil is previously mixed with 10% of a lead-manganese drier.

The results of an examination of tobacco seed oil, prepared on a large scale by the extraction of Dalmatian tobacco seed, have been published by K. Preissecker and H. Brezina.[28] The average yield of oil was 35·4% and the residue, which contained a relatively high percentage of nitrogen, might be suitable for cattle food. The oil had the following characteristics: Sp. gr. 0·9250 at 15° C.; acid value 9·5; saponif. value 196·4; iodine value 131·6. This iodine value is considerably higher than that already recorded for tobacco seed oil.

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[25] *J.*, 1920, 49T.

[26] *J.*, 1920, 153T.

[27] *Paint Manufrs. Assoc. U.S.*, *Circ.* 75 ; *J.*, 1920, 105R.

[28] *Fachl. Mitt. Oesterr. Tabakregie*, 1917, No. 4 ; *J.*, 1920, 71A.

H. Thoms,[29] by hot expression of the seeds of the mountain elder, *Sambucus racemosa, L.*, has obtained 30% of a drying oil consisting essentially of the glycerides of linolic, linolenic, and oleic acids and possibly isolinolenic acid together with palmitic and stearic acids. The following characteristics were obtained as the result of the examination of eight samples of the oil of different origin: Sp. gr. 0·9242–0·9439 at 21° C.; $n_D^{20} = 1{\cdot}47967$; acid value 3·07–29·24; saponif. value 186·9–198·1; iodine value 156·3–177·4. These figures are markedly different from those already published for this oil. The fruit oil is very different from the seed oil, a sample giving sp. gr. 0·9214 at 21° C.; solidification pt. -4° C.; acid value 5·59; saponif. value 196·5; iodine value 98·6. On heating the oil to 200° C. its toxic properties are destroyed.

O. von Friedrichs[30] has recorded the following figures for the oil obtained from the seeds of *Pinus sylvestris L.*: Sp. gr. 0·9307; solidf. pt. -30° C.; $n_D^{18} = 1{\cdot}4714$; acid value 0·92; saponif. value 190·7; Hehner value 94·75; Reichert-Meissl value 0·79; iodine value (Hanus) 159·2. The oil, which is of light yellow colour, mobile, and nearly odourless, contained 1·29% of crude phytosterol (m.p. 135° C.). The fatty acids consisted of about 3% of solid acids (palmitic acid with 5% stearic acid) and 97% of liquid acids (36·2% oleic, 56·2% linolic, and 7·6% linolenic acid).

Fir-seed-oil, extracted by the above author from the seeds of *Pinus abies L.*[31] by means of ether, is a pale yellow, mobile oil having a bitter taste, recalling that of turpentine, and a faint aromatic odour. It had the following characteristics: Sp. gr. 15° C. 0·9295; solidif. pt. -26° C.; $n_D^{18} = 1{\cdot}4801$, $n_D^{40} = 1{\cdot}4718$; acid value 1·0; saponif. value 191·8; iodine value (Hanus) 154; Hehner value 92·65; Riechert-Meissl value 1·06. The oil contained 91·6% of non-volatile fatty acids composed of 0·7% of palmitic acid and 99·3% of unsaturated acids (oleic 42·75, linolic 49·55, linolenic 7·7%).

Cockle-burr oil, which is obtained from the kernels contained in the burrs of *Xanthium echinatum,* has been examined by L. B. Rhodes.[32] The kernels, which amounted to 30·69% of the burrs, contained oil, 29·78–29·89%; moisture, 6·95–7·22%; crude protein, 40·34–40·53%; crude fibre, 2·47–2·58%; ash 5·42%. When cold-pressed they yielded a drying oil which had a pleasant odour and nutty flavour. It had the following characteristics: Sp. gr. at 15·5° C. 0·9251; $n_D^{15.5} = 1·4773$; Zeiss butyrometer reading at 20° C. 1·4771, 40° C. 1·4691; solidif. pt. –18·0° C.; iodine value (Hanus) 140·8; saponif. value 190·2; Reichert-Meissl value 0·233; Hehner value 89·7; acetyl value 10·6; m.p. of fatty acids 19·0° C. The kernel meal and press cake were both highly toxic to guinea pigs. In general properties the oil closely resembles that obtained from others of the *Xanthium* species.

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[29] *Ber. deuts. Pharm. Ges.*, 1919, **29**, 598; *J.*, 1920, 198A.

[30] *Svensk. Farm. Tidsk.*, 1919, **23**, 445, 461; *J.*, 1920, 304A.

[31] *Svensk. Farm. Tidsk.*, 1919, **23**, 500; *J.*, 1920, 304A.

[32] *J. Amer. Chem. Soc.*, 1920, **42**, 1507; *J.*, 1920, 604A.

H. A. Gardner and P. C. Holdt[33] have examined a specimen of chia oil prepared from the seeds of *Salvia Hispanica*. The seeds were of Mexican origin and contained 30·5% of a light amber coloured oil which had the following characteristics:—Sp. gr. at 15·5° C. 0·9338; acid value 0·6; iodine value 192·2; saponif. value 192·2; unsaponifiable matter 0·8%; $n_D^{25} = 1·4855$. The authors state that it exhibits the peculiar property, also possessed by perilla oil, of "creeping" into droplets when exposed to the air in film form and is therefore unsatisfactory as a drying oil in its natural state. This defect of both oils may be completely removed by heating them to 260° C. for a short time.

It is commonly believed that stillingia oil, obtained from the kernels of *Stillingia sebifera*, possesses toxic properties[34] and that danger attends the use as an edible fat of Chinese vegetable tallow which is obtained from the mesocarp of the seeds. H. S. Bailey[35] has prepared a quantity of the oil from seeds grown in South Carolina where the plant is common. The characteristics of the oil were normal in all respects and on feeding it to rabbits no toxic properties whatever were observed, it being stated by Dr. Salant of the Pharmacological Laboratory of the United States Bureau of Chemistry that it appears to have the same effect as other fatty oils. It is therefore concluded that there need be no fear of poisoning from the use of foods of commercial Chinese vegetable tallow, which are often contaminated with this oil. It is probably owing to the presence of small amounts of the kernel oil, which possesses marked drying properties, that the tallow from the mesocarp, even after careful purification, soon becomes bitter and of a disagreeable odour.[36]

SEMI-DRYING AND NON-DRYING OILS.

The composition of the fatty acids obtained from a refined oil from Sea Island cottonseed is stated by G. S. Jamieson and W. F. Baughman[37] to be, myristic, 0·3%; palmitic, 20%; stearic, 2%; arachidic, 0·6%; oleic, 35·2%; linolic, 41·7%. The separation of the saturated fatty acids was carried out by fractionating the methyl esters under reduced pressure and subsequently crystallising the products of hydrolysis of each fraction. It is to be noted that a small amount of stearic acid is stated to be present in the oil, although this has been the subject of much dispute in the past.[38] Although linolenic acid is not mentioned as a constituent of the oil, it should not be assumed that this holds good for cottonseed oil from all varieties of cottonseed since some samples of Indian cottonseed oil yield a small proportion of ether-insoluble polybromides.

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[33] *Paint Manufrs. Assoc. U.S., Circ.* 105 and 106; *J.*, 1920, 789A.

[34] Bolton and Revis, "Fatty Foods, their Practical Examination," p. 171.

[35] *Cotton Oil Press*, Nov., 1920, p. 50.

[36] Diedrichs, *Z. Unters. Nahr. Genussm.*, 1914, **27**, 132.

[37] *J. Amer. Chem. Soc.*, 1920, **42**, 1197; *J.*, 1920, 521A.

The composition of the mixed fatty acids obtained from a sample of arachis oil (iodine value 86·1) is stated by A. Heiduschka and S. Felser[39] to be, arachidic acid, 2·3%; lignoceric, 1·9%; stearic, 4·5%; palmitic, 4·0%; oleic, 79·9%; linolic, 7·4%. The oleic acid may have included a small quantity of hypogæic acid. The above figures are in close agreement with those hitherto accepted as expressing the composition of this oil.

A. Fercnez[40] has examined the oil obtained from the seeds of *Cnicus benedictus*, which is odourless and tasteless when cold-pressed, but dark brown when hot-pressing is employed. The oil content of the seeds varies from 24·4 to 28·3%. The oil had the following characters:—Sp. gr. at 15° C., 0·9262; acid value, 1·2; refrac. index, 1·47178; saponif. value, 191; iodine value, 141; Hehner value, 95·75; Reichert-Meissl value, 2·53. The liquid fatty acids consisted of about 74% oleic and 26% of linolic acids, and the solid acids of 40% stearic and 60% palmitic acid.

The cucurbitaceous plant *Momordica cochinchinensis* is common in Bengal, the Philippine Islands, etc. Its seeds, as reported by C. E. Corfield and E. Caird,[41] yield 63·3% of kernels which contain 47% of a greenish coloured fat. It has the following characteristics:—M.p. 28°–32° C.; $n_D^{40}=1{\cdot}495$; acid value, 1·9; saponif. value, 155·2; iodine value, 23·4. *Fatty acids*: m.p., 46°–51° C.; solidif. pt. 44°–42° C.; neut. value, 188·3; iodine value, 40. On being slowly heated to 200°–240° C. the fat is polymerised, being converted into a thick greenish brown oil which has semi-drying properties.

The oil from another cucurbitaceous plant, the hubbard squash (*Cucurbita maxima*), is reported by W. F. Baughman and G. S. Jamieson[42] to have the following characteristics:—Sp. gr. at 25°–25° C., 0·9179; $n_D^{25}=1{\cdot}4714$; iodine value (Hanus) 121·0; Reichert-Meissl value 0·37; acetyl value 94·66. The oil contains the glycerides of palmitic acid (13%), stearic acid (6%), arachidic acid (about 0·04%), oleic acid (37%), and linolic acid (44%).

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[38] Lewkowitsch, "Chem. Tech. and Anal. Oils, Fats, and Waxes," 1914, Vol. **2**, p. 305.

[39] *Z. Unters. Nahr. Genussm.*, 1919, **38**, 241; *J.*, 1920, 272A.

[40] *Arch. Pharm.*, 1919, **257**, 180; *J.*, 1920, 71A.

[41] *Pharm. J.*, 1920, **104**, 43; *J.*, 1920, 163A.

[42] *J. Amer. Chem. Soc.*, 1920, **42**, 152; *J.*, 1920, 417A.

It has been frequently stated that, during the war period, yeast fat was prepared in considerable quantity in Germany, where it is said to have been used for culinary purposes. Examined by I. S. MacLean and E M. Thomas[43] it is reported as being a brown liquid which contains 25–45% of unsaponifiable matter, which would seem to make it an undesirable material for dietetic purposes. Palmitic, oleic, and linoleic acids have been identified in it and there is evidence also of lauric and arachidic acids. Up to 20% of a sterol, probably ergosterol, has been found in it, partly in the free state and partly as fatty acid esters.

J. H. Shrader[44] gives an interesting account of American practice in the crushing of castor seeds. Practically the whole of the castor oil normally consumed in the United States (about 8000 tons) is locally crushed from imported seed. During 1917-18, however, the enormously increased use of castor oil for the lubrication of aero engines caused a rise in the import of seed to nearly 30,000 tons, of which 60% came from India, 19% from South America, and 8% from the West Indies. Castor seed was formerly grown in the United States, but owing to foreign competition cultivation ceased about 1900. The circumstances surrounding the increased demand just mentioned, revived local production so that in 1918 no less than 5750 tons of seed was raised. With the cessation of war and the increased world production of seed the prospects of castor seed as a permanent American crop are doubtful. Crushing is carried out in the well-known manner in cage presses, but large quantities are also pressed in continuous presses of the Anderson expeller type. The unsatisfactory results obtained in early attempts to use these machines are attributed to excessive wear caused by the hard seed husks on the cast steel used in the construction of earlier machines. The cast steel has now been replaced by case-hardened steel. Expellers having three worm-flights on the pressing screw are satisfactory and comparatively low pressures are employed.

Undecorticated seed gives a green oil which is not acceptable to the trade, and as decorticated seed is too soft to be worked in an oil expeller, arachis husks are added to provide a fibrous binder. The cake from the expellers contains 12–15% of oil which is removed by extraction in stationary or rotating extractors, the latter being favoured. The packing which is apt to occur in stationary extractors can be obviated by placing a layer of husks on the floor of the extractor after covering the floor with burlap between wire netting, and introducing the solvent from the bottom instead of from the top. The oil can be refined by blowing steam through it, thus coagulating albuminous matter which can be filtered off. Refining with alkali is troublesome as emulsions are easily formed, especially with the more acid oils. Bleaching is usually effected by treatment at 93° C. for about ½ hour with 2–4% of fuller's earth, followed by 0·2–1·5% of decolorising carbon and subsequent filtration. No. 3 quality oil cannot be satisfactorily bleached, and this is attributed to the fixation of the colour by heat and the presence of iron salts in the oil.

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[43] *Biochem. J.*, 1920, **14**, 483 ; *J.*, 1920, 640A.

[44] *U.S. Dept. Agric., Bull.* 867, 1920 ; *J.*, 1920, 392R.

SOLID FATS.

Schleichera trijuga, the seeds of which are the source of macassar oil, is widely spread throughout India, Malaya, and the East Indian Archipelago. In view of its utility as a timber tree the study of the seeds by N. N. Sen-Gupta[45] is not without importance. The cyanogenetic character of the seed is a strong deterrent to its use as a source of oil owing to the danger which attends the use of the cake for cattle food. That this danger is great is made evident by the fact that the author obtained nearly 0·4% of hydrocyanic acid by hydrolysis of the crushed seed at 25° C. By extracting the fat with anhydrous solvents the enzyme is destroyed, but since the glucoside remains unattacked, the safe use of the residue as a cattle food depends upon non-admixture with any other food which contains an enzyme capable of hydrolysing the glucoside. Experiments carried out with such foods as silage, hay, grass, and roots indicate that cyanogenesis is most marked with foods having a pronounced acidity. Wet and dry heat are also found to have an inhibitory effect and it is suggested that dry heating is worthy of most consideration on account of its practicability and simplicity of application.

The fat obtained from the seeds is a yellowish-white solid having a pleasant smell. The following characteristics, which in large measure confirm those already published, were determined:—Sp. gr. 99°/15° C., 0·86; m.p., initial 21° C., complete transparency 31° C.; solidif. pt. 29°–18° C.; saponif. value, (A) 229·1, (B) 214·4, iodine value (A) 52·4, (B) 55; $n_D^{21} = 1·46757$; $n_D^{27} = 1·46655$; $n_D^{31.5} = 1·4646$: acid value 13·06.

WAXES.

The composition of ghedda or East Indian wax has been investigated by A. Lipp and E. Casimir,[46] who state that it contains approximately 48% of ceryl alcohol; 7% of hydrocarbons (5% heptacosane, 2% hentriacontane, with traces of a hydrocarbon of low m.p.), 24–25% of hydroxymargaric acid, m.p. 55°–56° C., 1·5–2% of a hitherto unknown hydroxymargaric acid, m.p.

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[45] *J.*, 1920, 88T.

[46] *J. prakt. Chem.*, 1919, **99**, 256; *J.*, 1920, 163A.

71°–72° C., 9–10% of margaric acid, 8–9% of palmitic acid, 2% of "ghedda" acid, and 1% of cerotic acid, with traces of formic, acetic, and butyric acids and tarry matter. "Ghedda acid," m.p. 94°–95° C., which is given the provisional formula $C_{34}H_{66}O_2$, occurs, along with cerotic acid, mainly in the free condition, the other acids being present in the wax as their ceryl esters.

J. E. Q. Bosz,[47] who has examined a sample of sugar-cane wax extracted from the defecation mud of a Java sugar factory, states that it had m.p. 60°–62° C., acid value 47·3, and saponif. value 177. The fatty acids obtained after saponification had m.p. 54° C. and appeared to be an eutectic mixture of palmitic and stearic acids. Cholesterol was absent. In the liquid obtained on steam-distilling the product of saponification, myricyl alcohol, and caproic and formic acids were identified.

A. Heiduschka and M. Gareis[48] state that carnauba melissyl alcohol and beeswax melissyl alcohol are not identical, their formulæ having been determined as $C_{30}H_{61}OH$ and $C_{31}H_{63}OH$ respectively. Melissic acid from the first-named had m.p. 90° C. whilst that from the latter melted at 88·5° C.

HARDENED FATS.

The hydrogenation of oils in presence of a catalyst has become so well established as an industry that few of the numerous patents which have been published during the past year exhibit such novelty as to call for special comment. They are mainly concerned with such details as methods for the revivification of spent catalyst and modifications of the plant employed in the process, which is now constructed on well established lines. Patents covering the preparation of the nickel catalyst used in the process are numerous, their chief aim being to increase activity, generally by controlling the conditions under which the metal is reduced from its oxides or other compounds. A distinct departure from ordinary practice is indicated by the method patented by B. W. Elder[49] and more fully described by W. D. Richardson.[50] This method establishes the fact that reduction at comparatively low temperatures is not essential to high activity since such a catalyst can be prepared from block nickel by pulverising it by means of abrasives, if care is taken to prevent oxidation of the subdivided metal by carrying out the abrasion under oil, or better water, which is said to permit of the production of more finely-divided metal. Ball or tumbler mills which contain quartz, pumice, or other similar abrasives are suitable for the operation. The activity curve of the catalyst shows a considerable rise at the commencement of hydrogenation, which lasts for some time before it reaches its peak and declines.

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[47] *Arch. Suikerind. Nederl.-Indie*, 1920, **28**, 974; *J.*, 1920, 825A.

[48] *J. prakt. Chem.*, 1919, **99**, 293; *J.*, 1920, 163A.

[49] U.S.P. 1,331,903–1,331,906; *J.*, 1920, 305A.

[50] *Chem. and Met. Eng.*, 1920, **22**, 793; *J.*, 1920, 459A.

A. S. Kass[51] suggests that the catalytic activity of the oxides of nickel in the hydrogenation of oils at 255°–260° C. as used by Bedford and Erdmann[52] depends on the method used to prepare them and that their activity is considerably stimulated by the presence of small quantities of platinum. He further states that the use of a weak catalyst like nickel sesquioxide gives clear opportunity for observing that hydrogenation proceeds upon accepted lines of chemical activity, since the further a double linkage is from the carboxyl group the more difficult is it to reduce and the greater is the tendency to polymerisation.

T. Arentz[53] confirms the observation of C. W. Moore[54] that iso-oleic acid is formed during the hydrogenation of liquid oils, pointing out that the relationship between their physical and chemical constants is not the same as that of the natural fats.

Considerable attention is now being given to the mechanism of hydrogenation reactions from the theoretical point of view.

R. Thomas,[55] employing a closed apparatus, has studied the rate of hydrogenation of olive oil, and gives a mathematical analysis of the results based upon the unimolecular mass action equation, which allows for the simultaneous proceeding of the two hydrogenations—that of linolein and of olein. Broadly, he considers that the process is best explained on the radiation hypothesis, the prime action being the adsorption, solution, or incipient combination of hydrogen in or with the nickel; the olein is then attacked by the nickel-hydrogen solution or complex in accordance with the radiation theory—the action which gives rise to the unimolecular curves is apparently this latter change.

E. F. Armstrong and T. P. Hilditch[56] have published results which lead to a somewhat different interpretation of the procedure. Working in an open apparatus, *i.e.*, in one in which the unabsorbed hydrogen passes freely and continuously away from the acting system, they find that unsaturated fats containing mixtures of olein and less saturated glycerides than olein gave characteristic curves, more nearly a series of two straight lines than a combination of two unimolecular actions, the first (almost linear) segment corresponding to the portion of the process in which analysis of the product has shown that the main action is transformation of less saturated glycerides to olein, accompanied by very little conversion of olein to stearin. The second portion is not so straight, and covers the part of the action in which olein and iso-olein are passing to stearin.

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[51] *Przemysl Chem.*, 1920, **4**, 39; *J.*, 1920, 755A.
[52] *J.*, 1913, 611.
[53] *Chem.-Zeit.*, 1920, **44**, Rep., 67; *J.*, 1920, 304A.
[54] *J.*, 1919, 320T.
[55] *J.*, 1920, 10T.
[56] *Proc. Roy. Soc.*, 1919, A **96**, 322; *J.*, 1920, 163A.

A later communication[57] extends this study to suitably pure compounds (ethyl cinnamate, anethol, etc.) where it is found that the linear character of the absorption of hydrogen/time curves becomes very definite, and it is concluded that the action measured was the formation of a compound of an indefinite nature between the catalyst and the unsaturated compound.

Ultimately, these authors consider, the mechanism of hydrogenation is to be explained by this primary interaction between catalyst and unsaturated compound, the complex so formed being decomposed by hydrogen ; the hydrogen is also to be regarded as coupled with the nickel, both hydrogen and unsaturated compound being considered as having some affinity for the nickel.

This hypothesis is precisely the same as that adopted by H. E. and E. F. Armstrong[58] to explain the linear nature of the curves expressing the course of enzymic hydrolysis.

These authors also showed how the linear hydrogenation curves are transformed into unimolecular curves (i.) by the presence of a substance which slowly combines with the catalyst to form a permanent compound (a case of catalyst poisoning) and (ii.) by the accumulation of gaseous impurities in the gas-space above the acting system (notably when working in a closed apparatus) which affects the otherwise constant concentration of hydrogen above the liquid. As predicted by this theory, they also found that hydrogen could, under suitable conditions, be transferred from a saturated compound to an unsaturated one in the liquid state in presence of nickel (*e.g.*, from cyclohexanol to methyl cinnamate).

W. C. McC. Lewis[59] has examined Thomas' explanation of the hydrogenation of olein somewhat critically, without, however, adducing any further experimental evidence. His paper does not seem to assist materially in the elucidation of the mechanism of the process, but it is concluded that in the hydrogenation of olein and of similar substances adsorption of the unsaturated compound on the metal does not take place, the adsorption being restricted to the metal-hydrogen compounds.

W. D. Collins and W. F. Clarke[60] report the results of extended works experiments to replace the palm oil used in the tinplate industry with hydrogenated oils. The experiments showed that a satisfactory hydrogenated fish oil might be obtained and a continuous trial over twelve weeks showed somewhat better results with hardened cottonseed oil than with palm oil ; less oil was used but no saving of tin was effected.

[57] *J.*, 1920, 120T.

[58] *Proc. Roy. Soc.*, 1913, B **86**, 561.

[59] *Chem. Soc. Trans.*, 1920, **117**, 623.

[60] *J. Ind. Eng. Chem.*, 1920, **12**, 152. *J.*, 1920, 268A.

PAINTS, PIGMENTS, VARNISHES, AND RESINS.

By A. de Waele, A.I.C.,

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The period that has elapsed since the appearance of the Reports for 1919 has been fruitful in the publication of papers dealing with investigations on paint and varnish products by what in these industries has hitherto proved an unorthodox method of attack. Whilst in the past the elucidation of the complex physical and chemical reactions obtaining in products containing drying oils has been undertaken on the basis of pure chemical research, the recent application of the more academic methods of the physicist is significant in its promise of lifting the paint and varnish industry out of its condition of empiricism.[1] It is regrettable that the drying oil products, considered from the standpoint of their condition as colloids, show such a remarkable paucity of published work,[2] in spite of the apparently attractive field of investigation which the researcher should find at his disposal.

The formation in 1918 of The Oil and Colour Chemists' Association, a body devoting itself entirely to problems connected with the paint and varnish industries, and the membership of which practically represents all the chemists engaged in these industries, has resulted in the publication of much matter that would by reason of its specialised nature have been withheld from other bodies of more catholic interests. Several interesting publications have appeared during the year under the auspices of the Paint Manufacturers' Association of the United States and the National Varnish Manufacturers' Association. Whilst such deal with much useful matter relating to paint and varnish technology, and indeed furnish a lesson of altruism to the more secretive and conservative interests in this country, more work on the purely scientific side is to be desired, inasmuch as the publication of such would in no way offend the susceptibilities of the conservators of "trade secrets."

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[1] *J.*, 1919, 2R.

[2] *Third Report on Colloid Chemistry*, pp. 102-110.

PROPERTIES AND APPLICATIONS OF THE DRYING OILS.

The changes which occur in drying, semi-drying, and marine-animal oils on long storage at ordinary temperatures in indirect light have been examined by H. A. Gardner.[3] In almost every instance a loss in iodine value was recorded, whilst the oils increased in sp. gr., acid value, and saponification value. A decrease in acid and saponification values in rosin oil was attributed to the separation of a precipitate of acid character. The increases in acid values were very marked in the case of the marine-animal oils. Sterilisation of and removal of moisture from the oils had a marked effect in inhibiting changes, which are thus attributed to autohydrolysis of the glycerides. The same author and T. M. Rector[4] have found that the oxygen in the space above the liquid in a sealed can of paint or varnish is completely absorbed in a period of two weeks. In the light of an earlier paper of Gardner[5] a paper by A. de Waele[6] on the factors affecting the oxygen absorption of linseed oil is of interest. This author submitted samples of raw, variously siccatised, and polymerised linseed oils to atmospheric oxidation on filter papers in both daylight and darkness, noting the daily variations in weight together with atmospheric conditions of hygroscopicity (pressure of water vapour and relative humidity). The results when plotted as increase in weight/time curves, showed in their mean path in all cases but that of the polymerised oil, the typical sinuous curve noted by earlier observers. In addition, however, wavering of the curves in sympathy with the pressure of water vapour readings was shown, some additive effect of the relative humidity curve being also present. The latter effect was more marked in the case of the oxidations in darkness. It is concluded that the wavering of the curves is due to two effects: the decomposition of peroxide by moisture on the one hand tending to cause losses in weight, and the pressure of water vapour present in the atmosphere acting in a contrary direction to inhibit formation of decomposition products engendered by the former action. A noteworthy point is the similarity of path followed by both the raw and variously siccatised oils for some time after completion of the first "inductive" period, a somewhat remarkable finding in view of the distinction by R. S. Morrell[7] of driers into oxidising and polymerising classes. The well-known relative stability of polymerised oil in practice was also clearly borne out by a study of the curve from this oil, in the absence of the latter part of the S of the curve over a period of 133 days.

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[3] *J. Ind. Eng. Chem.*, 1919, **11**, 759; *J.*, 1919, 912A.

[4] *Circ.* 103, *Paint Manufrs. Assoc. U.S. and Nat. Varnish Manfrs. Assoc.*; *J.*, 1920, 605A.

[5] *Circ.* 70, *Paint Manufrs. Assoc. U.S.*; *J.*, 1919, 832A; *Ann. Repts.*, 1919, **4**, 303.

[6] *J.*, 1920, 48T.

[7] *Chem. Soc. Trans.*, 1918, **113**, 113; *J.*, 1918, 130A.

The influence of light of different wave-lengths on the drying of varnishes has been investigated by H. Wolff,[8] who concludes that light of short wave-length induces a rapid oxidation on the surface and also polymerisation in the inner layers, both effects proceeding at the same rate, whilst light of long wave-length of low actinic value results in a greater rapidity of oxidation taking place in the surface than polymerisation in the inner zone. Alterations in volume in the different zones with consequent production of shrivelling thus results from exposure to yellow, orange, or red light during drying. Wolff's conclusions are criticised by M. Ragg,[9] who points out that a higher rate of oxidation with a reduced rate of polymerisation would induce cracking in contradistinction to shrivelling. He offers the alternative hypothesis of the filtration of the ultra-violet rays in the surface, thereby transmitting only light of low actinic value to the inner zones, but whilst pointing out the necessity of consideration of possible thermal effects, does not make himself clear as to his interpretation of the mechanism of shrivelling. H. Wolff,[10] in replying to Ragg's criticisms, remarks that red light does not actually accelerate the rate of oxidation of varnish but induces a slight retardation of surface oxidation whilst considerably retarding polymerisation in the inner layer; light of short wave-length on the other hand allows oxidation and polymerisation to proceed at nearly equal rates. A final contribution to the discussion by H. Vollmann[11] suggests that red rays act exclusively by development of heat in both inner and outer layers, this effect influencing the polymerisation of the inner layers. The cause of shrivelling in varnish and oil films needs more investigation particularly in respect to the special occurrence of this phenomenon in products rich in China wood oil. The present writer thinks a possible confirmation of Wolff's hypothesis in that unequal rates of oxidation in surface and under layers are ultimately responsible for shrivelling, might be afforded by the suggestion that the reaction $AO_2+A=2\,AO$, *i.e.*, the transmission of oxygen from peroxide in the surface to unoxidised glyceride in the lower layer with formation of normal oxidised product, is not complete in some cases. An extension of the hypothesis would be that oxidation of such an oil as linseed would have for its primary effect the formation of a peroxide of the more unsaturated glyceride (linolenin):—$A+O_2=AO_2$; at the completion of such reaction the linolenin peroxide would then transmit its excess oxygen to the less saturated glyceride (linolin), thus :—$AO_2+B=AO+BO$. The absence of any glyceride other than elæomargarin in China wood oil would thus account for the non-occurrence of the second reaction in this case.

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[8] *Farben-Zeit.*, 1919, **24**, 1119; *J.*, 1919, 915A.
[9] *Farben-Zeit.*, 1919, **24**, 1308; *J.*, 1919, 915A.
[10] *Farben-Zeit.*, 1919, **24**, 1389; *J.*, 1919, 915A.
[11] *Farben-Zeit.*, 1919, **24**, 1427; *J.*, 1919, 915A.

A valuable summary of our knowledge of the mechanism of the oxidation of drying oils and of the effect of driers is given by R. S. Morrell,[12] who draws attention to the necessity of the further consideration of the latter in terms of their surface effects as catalysts. Thus, in spite of Fokin's[13] statement that the velocity of oxygen absorption of an oil increases with the cube root of the concentration of the catalyst, Morrell suggests the substitution of the surface concentration of the catalyst as the active mass in the reaction, the rate of diffusion of the reactants to and from the surface being also considered. This author shows that the (air) surface tension of linseed oil is lowered by the presence of lead linoleate in a solution of 1·3% strength, manganese and cobalt linoleates, in concentrations of 1·4% and 4·96% respectively, slightly raising the values. In solutions of one-tenth these concentrations the differences are less marked, diminution of the concentration of the manganese and cobalt salts having very little effect on the surface tensions, whereas the reduction in surface tension in the case of lead linoleate is more marked with variation in the concentration. The full interpretation of Willard Gibbs' equation for surface adsorption is rendered difficult, by reason of the lack of knowledge of the rate of diffusion, depending as it does on the viscosity of the layer. The preliminary observations made by this author are, however, well supported by results in practice in so far that increasing drying power in a drying oil is obtained by increasing lead concentration, whilst the reverse obtains with manganese or cobalt beyond a certain limit.

F. Fritz[14] points out that the so-called thickening effect of magnesium compounds on drying oils is only partly attributable to the intrinsic effect of the metal, being derived mainly from polymerisation induced in the oil at the necessarily high temperature of solution. The losses incurred on heating various drying and semi-drying oils together with the corresponding sp. grs. of the products are tabulated in a paper by H. A. Gardner and H. Parks.[15]

F. Bayer und Co.[16] claim a substitute for linseed oil obtained by condensing or polymerising aldol, acetaldehyde, crotonaldehyde, or other aldehydes in presence of alkalis, sodium acetate, etc.

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[12] *J.*, 1920, 153T.

[13] *Seifens. Zeit.*, **34**, 821.

[14] *Chem. Umschau*, 1919, **26**, 199 ; *J.*, 1920, 121A.

[15] *Circ.* 95, *Paint Manufrs. Assoc. U.S.* ; *J.*, 1920, 495A.

[16] G.P. 317,731 ; *J.*, 1920, 377A.

J. Marcusson[17] describes the preparation and properties of "Voltol" oils prepared by blowing vegetable and marine animal oils followed by an electrical treatment inducing polymerisation.

New Drying Oils.

H. A. Gardner[18] describes "soft lumbang" and candlenut oils obtained from *Aleurites trisperma* and *A. moluccana* respectively, and calls attention to the similarity of the latter to linseed oil. An anonymous writer,[19] in reviewing Gardner's paper and an article in *The Times' Trade Supplement*[20] drawing attention to the value of the lumbang oils, suggests a somewhat greater resemblance of "soft lumbang" oil to tung oil and its inclusion together with the oiticica oil of Bolton and Revis[21] in a sub-group occupied by tung oil. H. A. Gardner[22] describes the properties and uses in paint and varnish of various blubber type oils and shows that while unsuitable as such as paint vehicles, they give satisfactory results when mixed with linseed oil or tung oil varnish. The same author and A. Reilly[23] describe the constants and properties of Yellow-tail fish oil from *Seriola dorsalis* This oil dries slightly more slowly than linseed oil but yields an improved product when mixed with an equal weight of raw linseed oil. The oils from king salmon, silver salmon,[24] and Channel cat-fish[25] are described by H. A. Gardner, and their employment as paint vehicles when suitably treated, referred to. The present writer would point to the fact that the interest stimulated in the United States on the subject of various fish and marine-animal oils must be considered less as a criterion of their possible value in comparison with the better-known vegetable drying oils, than as a result of the local availability of what are at present more or less waste products. The appearance on the English market some ten years ago of menhaden oil, in spite of the quantity then available, did not result in the general adoption of what must at best be regarded as an oil, the oxidation product of which possesses markedly inferior physical properties to linseed oil.

Natural Resins.

The properties and constants of the resin scraped from pine trees have been described by H. Salvaterra[26] who obtained two resins of distinctly different characteristics by fractional extraction. P. Nicolardot and C. Coffignier[27] [28] have examined and published the properties and constants of a number of very soft resins. A very full account of the Indian methods of preparation of gum shellac are given by C. H. Jones,[29] together with analyses of the crude lac and the different varieties of manufactured product. U.S. Navy specifications for shellac for use in pattern and varnish work and coating decks are included, together with a suggested specification for a pure shellac varnish suitable for either electrical work or coating the interior of explosive shells. The oleo-resin from *Hardwickia pinnata* is described by K. S. Iyer and J. J. Sudborough.[30] The volatile oil separated by distillation with superheated steam would appear to be caryophyllene, thus pointing to the resemblance of the product to copaiba balsam. The authors, however, do not state the optical rotation of the product. The oleo-resin of *Dipterocarpus indicus* is described by J. C. Mansukhani and J. J. Sudborough[31] as being intermediate in properties between that of *Hardwickia pinnata* and that of other *Dipterocarpus Sp.* which yield gurjun balsam, *a*-caryophyllene having been isolated as the nitrosochloride. The residual resin yields both spirit- and oil-varnishes of good quality, whilst the volatile oil possesses therapeutic properties similar to those of copaiba oil. E. H. Rennie, W. T. Cooke, and H. H. Finlayson have examined a new species of *Xanthorrhœa* resin[32] from Kangaroo Island and W. Australia. In common with other species, it contains *p*-coumaric acid or its ester and *p*-hydroxybenzaldehyde. By steam distillation from a strongly alkaline solution, the following additional substances amongst others were obtained: pæonal (2-hydroxy-4-methoxyacetophenone), hydroxypæonol, 1-citronellol, and a compound which was possibly methoxydiphenyl ether.

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[17] *Z. angew. Chem.*, 1920, **33**, 231, 234 ; *J.*, 1920, 755A.

[18] *Circ.* 75, *Paint Manufrs. Assoc. U.S.* ; *J.*, 1919, 952A.

[19] *J.*, 1920, 105R.

[20] *Times, Trade Suppl.*, Dec. 27, 1919.

[21] *Analyst*, 1918, 43, 251 ; *J.*, 1918, 430A.

[22] *Circ.* 74, *Paint Manufrs. Assoc. U.S.* ; *J.*, 1919, 953A.

[23] *Circ.* 86, *Paint Manufrs. Assoc. U.S.* ; *J.*, 1920, 304A.

[24] *Circ.* 92, *Paint Manufrs. Assoc. U.S.* ; *J.*, 1920, 494A.

[25] *Circ.* 93, *Paint Manufrs. Assoc. U.S.* ; *J.*, 1920, 495A.

[26] *Chem.-Zeit.*, 1919, **43**, 739 ; *J.*, 1919, 953A.

A raw material for use as a substitute for shellac is obtained by a method patented by H. J. Pooley and J. L. Strevens,[33] the outside portions of the grass-tree (*Xanthorrhœa*) or its crude resins being extracted with benzene or its homologues boiling below 180° C.

L. Paul[34] has continued his investigations on the autoxidation of colophony, having separated γ-pinic acid by precipitating an alkali solution of common rosin with hydrochloric acid. γ-Pinic

[27] *Bull. Soc. Chim.*, 1919, **25**, 579; *J.*, 1919, 954A.

[28] *Bull. Soc. Chim.*, 1920, **27**, 71; *J.*, 1920, 198A.

[29] *Chem. and Met. Eng.*, 1919, **21**, 715; *J.*, 1920, 121A.

[30] *J. Ind. Inst. Sci.*, 1918, **2**, 29; *J.*, 1920, 342A.

[31] *J. Ind. Inst. Sci.*, 1918, **2**, 37; *J.*, 1920, 342A.

[32] *Chem. Soc. Trans.*, 1920, **117**, 338; *J.*, 1920, 459A.

[33] E.P. 150,638; *J.*, 1920, 697A.

[34] *Kolloid Zeits.*, 1919, **25**, 241; *J.*, 1920, 198A.

acid melts at 75°–76° C. when freshly prepared, the melting-point rising to 88° C. in eight months. It is soluble in both water and petroleum. α-Pinic acid has a constant melting-point of 81°–83° C., whilst β-pinic acid melts at 98°–100° C.

A study of the composition of abietic acid from American rosin has been undertaken by D. Johansson[35] with a view to seeking evidence of its unsaturation and the presence in its molecule of the aromatic and hydroaromatic nuclei postulated by previous investigators. The degree of unsaturation as determined by the Hübl-Waller and Winkler iodine values leads to numbers being obtained which increased with the duration of the determination. Approximately the same values and relationships were obtained with *d*-pimaric acid and its dihydro-derivative. It is therefore suggested that the unreduced acids contain at least two non-equivalent double bonds. This author considers the presence of an aromatic or hydroaromatic nucleus to be now definitely established.

An account of the properties of "distilled colophony" or rosin pitch is given by L. Gerstacker.[36]

SYNTHETIC RESINS.

1. *Coumarone type.*

Although, judging from the literature published during the year, an increasing interest seems to be taken in paracoumarone resin, little of this seems to have been reflected in the paint and varnish trade of this country. The writer has formed the impression that paracoumarone resin will be found to agree very closely in behaviour with glycerin-rosin ester, a product which has been exceedingly slow to find general adoption, in spite of its value in varnish-making having been definitely established. The notorious conservativism of the varnish maker no doubt accounts for the latter to a large extent, the high price of ester-gum, however, also having precluded a more active interest in it. Paracoumarone resin, although referred to by some American writers as a common commercial product in the United States, does not appear to have been yet made commercially in England, although the writer is given to understand by an important firm of British manufacturers that they are shortly contemplating placing the product on the market at a price which will compare very favourably with that of the best grades of ester-gum.

The manufacture and applications of coumarone and paracoumarone resins are ably summarised in an article by W. W. King, F. W. Bayard, and F. H. Rhodes.[37] The particular value of the resin, which very closely simulates common rosin in appearance, lies in its neutrality and stability to chemical agencies. Resins of melting points below 125° C. are stated to be unsuitable for use in varnishes, owing to their persistent retention of solvent. The authors state that resins of melting-points between 125° and 145° C. are now commonly prepared and that there is every hope of products of still higher melting-point being obtained commercially. A method of manufacture of varnish is given which agrees very closely with the procedure for the manufacture of a varnish from ester-gum and China wood oil.

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[35] *Arkiv Kem., Min., Geol.*, 1917, **6**, No. 19; *J.*, 1920, 198A.

[36] *Farben-Zeit.*, 1920, **25**, 1170; *J.*, 1920, 418A.

[37] *J. Ind. Eng. Chem.*, 1920, **12**, 549; *J.*, 1920, 551A.

M. Ragg[38] gives some tests for the valuation of coumarone resins, and mentions *inter alia* their uses as substitutes for common rosin in the manufacture of explosives.

M. Darrin[39] claims the use of the resin obtained by polymerising solvent naphtha in admixture with a paint or varnish oil. The same worker[40] polymerises by heat the compounds of crude solvent naphtha and claims that he obtains thereby clear reddish products of m.pt. over 180° C. The Farbenfabr. vorm F. Bayer u. Co.[41] claims the use for varnishes etc., of linseed oil substitutes consisting of alkyl- or aralkyl-indene derivatives containing the double linkage of the cyclopentadiene ring. The Rütgerswerke A.-G.[42] claims the preparation of alcohol-soluble coumarone resins suitable for use in spirit varnishes by polymerisation of crude solvent naphtha in the presence of phenols. The use of polymerised resins of the coumarone or indene group with oil is claimed by G. W. Priest[43] as a composition for making linoleum, whilst A. A. Wells[44] claims the use of coumarone resin as a moulded electric insulator. G. Muth[45] emulsifies coumarone resin in aqueous emulsoids for use in paper-sizing. H. V. Dunham[46] obtains resins by passing vaporised di-enes over a heated contact mass.

The Deutsch-Luxemburgische Bergwerks- und Hütten A.-G., and S. Hilpert[47] [48] [49] add to a varnish containing coumarone resin, a resin separated in the purification of benzol and other coal-tar fractions by means of sulphuric acid. J. Schümmer[50] obtains pale drying oils by distilling *in vacuo* the acid resins from the purification of benzine.

[38] *Farben-Zeit.*, 1919, **25**, 16, 61, 105, 145; *J.*, 1920, 273A.

[39] U.S.P. 1,315,658; *J.*, 1919, 834A.

[40] U.S.P. 1,326,579; *J.*, 1920, 165A.

[41] G.P. 305,515; *J.*, 1920, 165A.

[42] G.P. 302,543; *J.*, 1920, 307A.

[43] U.S.P. 1,334,049 and 1,334,050; *J.*, 1920, 342A.

[44] U.S.P. 1,332,860; *J.*, 1920, 340A.

[45] G.P. 316,345; *J.*, 1920, 361A.

[46] U.S.P. 1,324,649; *J.*, 1920, 164A.

[47] G.P. 319,011; *J.*, 1920, 577A.

[48] G.P. 319,010; *J.*, 1920, 577A.

[49] G.P. 320,808; *J.*, 1920, 665A.

[50] G.P. 320,255; *J.*, 1920, 633A.

2. *Bakelite type.*

Progress on the manufacture of phenolic condensation products has been principally in the direction of the application of knowledge of the conditions of reaction to the attainment of specific properties in the final product. Thus, solubility to the point of the obtainment of alcohol- and oil-soluble resins is claimed to be obtained by the restriction of reacting phenol to *o*-cresol. M. Ragg, in a review of the properties of commercial formolite resins,[38] refers to " issolin " as a resin soluble in alcohol and suitable when in alcoholic solution as an air-drying varnish, and " albertole," a resin soluble in fatty oils and other solvents. It is improbable, however, that these products will enter the field of interest of the varnish-maker for some time as their cost of production places them out of consideration when compared with the naturally occurring resins.

W. Esch[51] condenses phenols or *o*- and *m*-cresols or their derivatives with an aqueous solution of an aldehyde in presence of benzoates or salicylates as catalysts.

W. T. Robinson-Bindley, A. W. Weller, and E. Dulcken[52] obtain celluloid or vulcanite substitutes from gaseous *o*-, *m*-, or *p*-cresol and formaldehyde, employing sodium sulphite as catalyst, subsequently incorporating camphene and nitrocellulose or cellulose acetate into the condensation product. The same patentees[53] claim to obtain spirit-soluble resins suitable for use as shellac substitutes by condensing *m*-cresol with formaldehyde; an oil-soluble product is obtained by employing *p*-cresol. K. Albert and L. Berend[54] prepare both soluble and fusible as well as insoluble and infusible condensation products from formaldehyde and *m*-cresol or its higher homologues in the absence of acids and alkalis. The Chem. Fabr. K. Albert and L. Berend[55] take advantage of the more rapid reactivity of the *m*-substituted phenols with formaldehyde to obtain more fusible resins. F. J. Robinson and the Damard Lacquer Co., Ltd.,[56] prepare a condensation product flexible at 120° C. from cresol, formaldehyde, ammonia, and castor or other oil. The Badische Anilin- und Soda-Fabrik[57] dissolve artificial resins from a formaldehyde-naphthalene condensation product in organic solvents and emulsify the solutions in soap solutions etc.

C. C. Böhler[58] produces an artificial resin by vulcanising anhydroformaldehyde-aniline with sulphur chloride. Artificial tanning substances are prepared by the Deutsch-Koloniale

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[51] G.P. 305,538; *J.*, 1919, 954A.

[52] E.P. 134,564 and 134,565; *J.*, 1920, 14A. E.P. 145,128; *J.*, 1920, 568A.

[53] E.P. 134,563; *J.*, 1920, 35A.

[54] G.P. 301,374; *J.*, 1920, 122A.

[55] G.P. 304,384; *J.*, 1920, 273A.

[56] E.P. 136,298; *J.*, 1920, 164A.

[57] G.P. 307,123; *J.*, 1920, 377A.

[58] G.P. 317,267; *J.*, 1920, 377A.

Gerb- und Farbstoff-Ges.m.b.h.[59] from aminohydroxynaphthalenesulphonic acids and formaldehyde. L. V. Redman, A. J. Weith, and F. P. Brock[60] treat a fusible phenolic condensation product with a phenolic body, a methyleneamine compound, and a filler to form a hard, resistant product. L. T. Richardson[61] produces a resinous moulded product in two stages of condensation. C. A. Nash[62] whilst obtaining an infusible body by two stages of hardening, employs a slowly volatile solvent for the condensation product in its fusible state together with a fibrous filler. L. V. Redman, A. J. Weith, and F. P. Brock[63] describe a process of obtaining a phenolic condensation product without the use of a catalyst and a method of preserving an infusible product of the transparent order from discoloration. An interesting inquiry was undertaken by E. Beckmann and E. Dehn[64] to determine the possible substitution of formaldehyde by furfuraldehyde in phenolic condensation products. Valuable data are given as to the effect of various phenols, catalysts, and fillers on the properties of the finished product.

ASPHALT, BITUMEN, AND PITCH.

Two very good accounts of the composition, properties, and examination of these products have been published during the past year. J. Marcusson[65] describes the characteristics of natural asphalt, fat distillation residues, and commercial products manufactured from the same and coal-tar pitch. The paper is valuable in giving a very full account of the methods employed for the detection of the various pitches in presence of each other. H. M. Langton[66] reviews the composition and properties of pitches and bituminous materials and gives an up-to-date bibliography of the subject, whilst publishing the constants of fat pitches from several sources. The various forms in which bitumens are used for the preparation of acid-proof coatings for concrete surfaces are given in a report by the Bituminous Materials and Cement Section, U.S. Bureau of Standards,[67] general specifications of each kind of material, and tests to ensure compliance with the specifications being given.

COPAL VARNISHES.

Progress in varnish technology during the past year has been mainly confined to attempts to apply physico-chemical methods of investigation. That many of the peculiar properties shown by varnish films cannot be explained on a purely chemical basis, but that the importance of surface effect needs to be considered, is pointed out by R. S. Morrell,[68] who gives a useful summary of present-day knowledge of the phenomena of varnish manufacture and application regarded from the standpoint of the colloid state. This writer tabulates the results of experiments on the permeability of various varnish, oil, and linoxyn films to water and to solutions of certain salts of the lyotrope series, and shows the influence of polymerisation in enhancing the water-resistance of linoxyn. The permeating effect of saline solutions appears to be to a degree inversely proportional to the concentration of the solution, but the metal-ion does not itself appear to penetrate into the film. The drop numbers of water and of salt solutions into an elastic varnish are also tabulated together with the increases in weight observed by immersion of the dried varnish films in the same saline solutions. Some definite connexion appeared to exist between the two figures recorded, low interfacial tensions, paradoxically enough, showing lower permeabilities of their dried films, although, as pointed out in the discussion, the determinations are not strictly comparable owing to the absence of volatile distillate in the dried film. The same author in his contribution to the Third Report on Colloid Chemistry[69] gives a very complete summary of the properties of oil, paint, resin, and varnish products regarded from the standpoint of physical and physico-chemical knowledge. Some further work by the same writer on the influence of adsorption in films of drying media has been dealt with under another heading.

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[59] G.P. 315,871 ; *J.*, 1920, 378A.
[60] U.S.P. 1,339,134 ; *J.*, 1920, 460A.
[61] U.S.P. 1,342,067 ; *J.*, 1920, 522A.
[62] U.S.P. 1,343,575 ; *J.*, 1920, 552A.
[63] U.S.P. 1,345,694 and 1,345,695 ; *J.*, 1920, 605A.
[64] *Sitzungsber. Preuss. Akad. Wiss.*, 1918, 1201 ; *J.*, 1920, 577A.
[65] *Mitt. k. Materialprüf.*, 1918, **36**, 279 ; *J.*, 1919, 453A.
[66] *Proc. Oil and Colour Chemists' Assoc.*, 1919, 7 ; *J.*, 1919, 354A
[67] *Chem. and Met. Eng.*, 1920, **23**, 287 ; *J.*, 1920, 664A.

Whilst on the subject of the colloid state ot varnish products, an interesting application of a method not hitherto applied to this class of product appears as a patent by the British Thomson-Houston Co., Ltd.,[70] who emulsify solvent-free stoving-japan with the aid of an alkali, the object to be treated being heated, immersed, and then stoved. Alternatively the object is immersed as anode, cataphoresis presumably resulting with deposition of the negatively-charged japan composition, the coated article being finally stoved.

The pursuit of methods for the analysis of copal varnishes and the interpretation of results to practical valuation still continues. W. T. Pearce[71] determines resin and oil by a close modification of Boughton's method, the proportion of China wood oil present in the latter being determined separately. Rosin is similarly determined separately by Wolff's esterification method. The chemical analyses are supplemented by a series of physical tests embodying sp. gr., viscosity, flowing properties, scratch test, elasticity of the dried film, and exposure test. The results tabulated do not show any very conclusive agreement between the laboratory and exposure tests. A. de Waele[72] points out that the valuation of varnish products may be misleading when analytical results are not interpreted by a varnish technologist, and gives a somewhat elaborate method of analytical procedure. The method, for the details of which the original paper must be consulted, embodies determination of unsaponifiable matter, petroleum-ether insoluble acids and unesterifiable acids, allocation of the fractions separated to gum-resin, rosin, and oil being determined by qualitative examination of a fraction not hitherto investigated by other observers. The calculation of results is somewhat intricate. This author finally applies additional physical tests and distinguishes between *chemical* weather-resistance which he defines as the intrinsic stability of the oil fraction under conditions of atmospheric exposure, and *physical* weather-resistance or the elasticity and hardness under the conditions of service. The former is claimed to be determined by noting the relative "corrosion" produced by allowing 20-volume hydrogen peroxide to evaporate spontaneously on the air-dried film. The paper concludes with suggested specifications for various classes of varnishes.

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[68] *Proc. Oil and Colour Chemists' Assoc.*, 1920, III., 16, 29-51.

[69] *Dept. of Sci. and Ind. Research, Brit. Assoc. for the Adv. of Sci.*, 1920, 102-113.

[70] E.P. 121,433 ; *J.*, 1919, 81A.

[71] *J. Ind. Eng. Chem.*, 1920, **12**, 552 ; *J.*, 1920, 551A.

The manufacture of a substantially neutral glycerin-rosin ester with the aid of tung-oil as esterifying catalyst, and named "tunga resin," has been described by H. A. Gardner and P. C. Holdt.[73] The properties and application of "tunga-resin" to varnish manufacture in conjunction with various drying oils are also described.[74] The novelty and usefulness of such a product, which shows an acid value (on the rosin content) of about 40, are questioned by the writer, since the particular value of commercial rosin esters on the market lies in the fact of their acid values not exceeding 3 or 4 units. The authors furthermore have not made out a case of catalysis for the tung oil in any but a mechanical direction.

A revival of a method which appeared some ten years ago in a series of patents by Kaempfe and by Waentig for making a varnish from fish oil, has been patented by A. Kronstein,[75] who distils fish oil *in vacuo*, the amount of distillate governing the special requirements of body of the finished varnish. Such a product, which depends for its drying properties on selective distillation of the stearin-containing glycerides and polymerisation of the residue, can be taken as being of fair value when the dark colour and high viscosity of the residue are not objectionable.[76]

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[72] *Proc. Oil and Colour Chemists' Assoc.*, 1920, **17**, 75.

[73] *Circ.* 101, *Paint Manufrs. Assoc., U.S.*; *J.*, 1920, 791A.

[74] *Circ.* 102, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 664A.

[75] G.P. 302,544; *J.*, 1920, 122A.

F. Bruggemann[77] claims to prevent oxidation of an impregnating varnish by addition of a reducing agent such as zinc dust. The Ballonhüllen-Ges.m.b.H.[78] add vulcanised castor or other oil prepared by the action of sulphur chloride, as an ingredient to render balloon varnish waterproof etc.

L. Singer and H. Kantorowicz[79] convert the extracts obtained by treating hydrocarbons with sulphurous acid into siccative products suitable as thickened drying oils. L. E. Andés[80] describes the types of varnishes used for papier-mâché ware. The Vereinigte Chem. Werke A.-G., K. Lüdecke, und L. Mamlock[81] prepare a varnish resin claimed to differ from furfuryl alcohol, by treatment of furfural with zinc etc. and a mineral acid. R. Koetschau, C. Harries, and E. Albrecht[82] employ ozonides of the unsaturated hydrocarbons of petroleum as substitutes for linseed oil varnish.

Driers.

Much of the matter relating to the influence of driers on the oxidation of oils has already been dealt with in the section on the properties of the drying oils[6, 7, 12]. The publication of experiments purporting to show the specific influence of the acidic radicle of metallic soaps appears to be less in vogue in consequence of the present-day recognition of the comparative insignificance of this latter in relation to the base. Two papers, however, have been published dealing with the physical properties of certain metallic soaps. M. d'A. Albuquerque[83] describes the preparation of a number of heavy metal oleates and stearates, the colours of their ethereal solutions, air-oxidation products, products of oxidation by hydrogen peroxide, and the stabilities of their peroxidised solutions. The absorption spectra of the (non-ionised) metals in ethereal solutions were also observed. P. Nicolardot and C. Coffignier[84] prepared a number of the fused metallic resinates commonly employed in varnish technology, noting the yields, apparent acid values, and solubilities in turpentine. These authors found the presence of small amounts of lime to be beneficial in assisting solution of other oxides and increasing the solubilities of the resultant products.

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[76] Private communication from J. W. Brisbane.

[77] G.P. 315,700 ; *J.*, 1920, 633A.

[78] G.P. 321,264 ; *J.*, 1920, 698A.

[79] G.P. 312,927 ; *J.*, 1919, 916A.

[80] *Farben-Zeit.*, 1919, **20**, 999 ; *J.*, 1919, 833A

[81] G.P. 307,622 ; *J.*, 1920, 273A.

[82] G.P. 323,155 ; *J.*, 1920, 757A.

[83] *Revista Chim. pura e appl.*, 1916, **1** ; *J.*, 1920, 240A.

[84] *Bull. Soc. Chim.*, 1920, **27**, 166 ; *J.*, 1920, 241A.

The Farbenfabr. vorm F. Bayer und Co.[85] claim the use of metallic compounds of 1.3-diketones or 1.3-ketocarboxylic acids as driers, giving in their specification examples of the lead, manganese, etc. compounds.

Varnish and paint solvents.

H. Wolff,[86] in dealing with the solvents employed for solution of synthetic resins, points out the increased viscosity of such resin solutions as addition of non-solvent induces a change from molecular to colloidal solution or even gel formation, and suggests that persistent softness of residual films resulting from exposure of resin solutions is to be accounted for by selective evaporation of the true solvent. Application of such hypothesis to copal varnish systems might, in the present writer's opinion, furnish interesting and useful information covering such phenomenom. The common statement, unsupported by conclusive evidence, is that the greater drying power of varnishes containing turpentine over those containing petroleum distillates is to be accounted for by the accelerating effect of the peroxides formed in the former case; it may be more probably attributable to the greater solvent power of the turpentine since the increased drying effect in this case is out of all proportion to the peroxidising influence to be expected.

The halogen absorption of turpentine has been studied by E. M. Taylor,[87] who shows that complete bromination to the tetrabromide $C_{10}H_{16}Br_4$ can be effected by the use of iodine tribromide in chloroform, complete absorption of halogen never resulting with Wijs' solution.

An account of the distribution of the Indian pine rosin (*Pinus longifolia*) in the Himalayas and the yield of rosin and turpentine therefrom is given in a short review.[88] Indian turpentine from *P. longifolia Roxb.*, has been examined by J. L. Simonsen.[89] *α*- and *β*-pinene, *d*-longifolene, and a terpene considered to be either Δ^3- or Δ^4-carene, in addition to a bicyclic terpene which was named *d*-carene, were separated.

A very exhaustive and detailed account of the French turpentine industry, including a description of the derivatives of French turpentine, has been given by A. Joly.[90]

A new class of paint solvents known by the name of "tetralin" and consisting of hydronaphthalenes has been described by H. Vollmann.[91] Tetralin consists of tetrahydronaphthalene whilst "tetralin extra" is a mixture of tetralin and "dekaline" or dihydronaphthalene. These products are stated to be serviceable turpentine substitutes of great solvent power and low volatility. "Tetralin extra" is claimed to act as an oxygen carrier. The use of these solvents for the extraction of resins, caoutchouc, sulphur, etc.,[92] or dried oil and varnish films[93] have been claimed by the Tetralin G.m.b.h.

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[85] G.P. 305,692; *J.*, 1920, 273A.

[86] *Farben-Zeit.*, 1920, **25**, 688; *J.*, 1920, 342A.

[87] *Analyst*, 1919, **44**. 401; *J.*, 1920, 72A

[88] *J.*, 1920, 201R.

[89] *Chem. Soc. Trans.*, 1920, **117**, 570; *J.*, 1920, 581A.

[90] *Proc. Oil and Colour Chemists' Assoc.*, 1920, **15**, 149.

[91] *Farben-Zeit.*, 1919, **24**, 1689; *J.*, 1920, 35A.

DOPES AND CELLULOSE VARNISHES.

The number of patents dealing with cellulose esters taken out since the publication of the last Reports appears to have been considerably less than during the previous period, an effect no doubt attributable to the main importance of dopes being in connexion with application to aircraft fabrics. The application of varnishes containing cellulose acetate to purposes where the tautening effect on fabrics is not a primary consideration is hardly to be expected in view of the high cost of the product. Thus there is reason to believe that in spite of the lower inflammability of cellulose acetate as compared with cellulose nitrate, there is little prospect of the displacement of the latter by the former in the cellulose ester varnishes commonly employed. In connexion with the fire-proofing of cellulose nitrate products, the use of 5–8% of ammonium phosphate or magnesium ammonium phosphate has been suggested.[94]

A general review of the history of cellulose acetate, its manufacture and properties, is given by E. C. Worden,[95] who appends a very complete bibliography of the literature and patent specifications dealing with this product. A. Fuchs[96] gives an account of the various materials used on planes and of the components used to confer waterproof, plastic, and fireproof properties on the dope film, and describes the methods of application of dopes, the drying of the films, and solvent recovery. H. J. H. Fenton and A. J. Berry[97] have investigated the possibilities of substitutes for acetone as a cellulose acetate solvent and find no objection to the use of esters or weak acids in so far as the effect on tensile strengths of the fabrics is concerned. These authors find a relationship between the dielectric constant and solvent action of a solvent. The viscosity of ether-alcohol solutions of cellulose nitrate has been investigated by W. H. Gibson and R. McCall[98] and the effect of partial substitution of the solvent by nitroglycerin.

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[92] G. P. 320,807; *J.*, 1920, 665A.

[93] G.P. 320,152; *J.*, 1920, 665A.

[94] *J.*, 1920, 201R.

[95] *J.*, 1919, 370T.

[96] *Chim. et Ind.*, 1920, **3**, 167; *J.*, 1920, 292A.

[97] *Proc. Camb. Phil. Soc.*, 1920, **20**, 16; *J.*, 1920, 624A.

[98] *J.*, 1920, 172T.

I. Masson and R. McCall[99] also publish results on the viscosities of cellulose nitrate in mixtures of acetone and water, and explain the anomaly of lowered viscosity with increasing non-solvent up to a limiting value, by the suggestion of selective adsorption of the solvent by the gel. G. J. Esselen, jun.,[100] gives an account of the manufacture of and the action of solvents on cellulose acetate and postulates a theory of affinity of the ester for hydroxyl groups to account for the solvent effect of non-solvents when in presence of alcohol. The preparation of cellulose phthalate has been described by H. A. Levey,[101] who identifies the ester as being of a composition represented by one molecule of acid to eight of cellulose, $C_6H_{10}O_5$; the ester is, however, practically insoluble in all the usual organic solvents. The Soc. Nauton Frères et de Marsac and T. F. Tesse[102] add metallic powders such as aluminium, bronze, copper, etc., to dope to permit addition of increased proportions of high boiling-point substitutes for camphor, to reduce inflammability and visibility, and to inhibit the injurious effects of the sun's rays. The same patentees [103] coat aeroplane fabrics with superposed layers of varnishes containing smoke black or Paris blue and a transparent red lake respectively to induce "invisibility." A. J. A. W. Barr and H. Lazell[104] employ a mixture of light-absorbing pigments with aluminium powder to inhibit the effect of ultraviolet rays and reduce visibility. The addition of boric acid to dope varnishes in the form of a solution in benzol is claimed by D. M. Sutherland and The Wall Paper Manufacturers, Ltd.,[105] to permit the use of more benzol, to fireproof, retard drying, and diminish the viscosity of the varnish, whilst Titanine, Ltd., and P. E. Bowles[106] add a small proportion of the same compound to permit long storage of dope without undue loss in viscosity. Other patents are those of J. M. Kessler,[107] who employs acetaldol as a constituent of cellulose acetate varnishes; C. Dreyfus, who claims lanoline[108] and drying oils[109] to render cellulose acetate films permanently plastic; F. Clouth[110] who employs anthracene oil in combination with cellulose acetate to increase elasticity and impart waterproof qualities. J. G Jarvis[111] produces a pyroxylin sheet of low inflammability by addition of cinchonine to an acetone solution of cellulose acetate, and in a later patent[112] reduces the inflammability of films of cellulose nitrate and cellulose acetate by addition of chloral hydrate and cinchonine. Vickers, Ltd., J. McKechnie. and A. Ryan[113] wholly or partially convert cotton or other fibre fabric into cellulose acetate previous to the application of dope.

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[99] *Chem. Soc. Trans.*, 1920, **117**, 819; *J.*, 1920, 641A.

[100] *J. Ind. Eng. Chem.*, 1920, **12**, 801.

[101] *J. Ind. Eng. Chem.*, 1920 **12**, 743; *J.*, 1920, 624A

[102] E.P. 126,989; *J.*, 1919, 531A.

[103] E.P. 131,369; *J.*, 1919, 759A.

[104] E.P. 131,641; *J.*, 1919, 834A.

[105] E.P. 131,082; *J.*, 1919, 834A.

[106] E.P. 136,927; *J.*, 1920, 164A.

[107] U.S.P. 1,303,563; *J.*, 1919, 531A.

[108] E.P. 127,615; *J.*, 1919, 531A.

[109] E.P. 127,678; *J.*, 1919, 531A.

[110] G.P. 319,723; *J.*, 1920, 568A.

[111] U.S.P. 1,349,156; *J.*, 1920, 653A.

PIGMENTS.

A considerable amount of interesting work dealing with the physics of pigments and paint systems has been undertaken during the past year, a great proportion having been published under the auspices of the Paint Manufacturers' Association of the United States. It is to be hoped that the results published will attract the attention of the more academic school of physicists in order that the problems connected with the paint industry may receive the consideration they deserve in relating to a particularly interesting class of non-aqueous colloid systems.

A method for determining the relative fineness of pigments has been worked out by H. A. Gardner,[114] who rubs the pigment with the finger across the grooves of an Edison disc phonograph record, the surface being then examined under the microscope. This author further suggests the possibilities of a count of the number of particles in a given weight of pigment by examining a gelatin suspension under the microscope in the cell of a hœmocytometer, but the present writer's experience would show the difficulty of such method on account of aggregation of the particles of many pigments taking place. W. K. Lewis and F. P. Baker[115] determine the thickness of a suspension of a pigment in a medium needed to diffuse completely the outline of the filament of an incandescent electric bulb and thereby obtain its "diffusing power," a figure very closely related to the degree of dispersion. R. L. Hallett[116] describes an instrument for determining the hiding power of paints, depending on the critical distance at which a pigment painted in stripes on a white card is uniformly illuminated when viewed through a specially designed ground-glass objective. A.H. Pfund[117] has designed an instrument named the "cryptometer" for determining the hiding power of pigments and paints, the principle of which appears free from objection and the application simple and rapid. The bulking values and yields of pigments and liquids in paints have been worked out and tabulated by H. A. Gardner and H. C. Parks.[118] The publication covers nearly all the commercial pigments used in American practice. H. A. Gardner and R. E. Coleman[119] determine oil absorptions of pigments by a method involving the use of simple laboratory apparatus. The figures obtained do not, however, conform to those found in grinding practice.

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[112] U.S.P. 1,354,401, *J.*, 1920, 719A.

[113] E.P. 142,615; *J.*, 1920, 482A.

[114] *Circ.* 90, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 342A.

[115] *J. Ind. Eng. Chem.*, 1920, **12**, 890; *J.*, 1920, 697A.

[116] Amer. Soc. Test. Mat., June, 1920; *J.*, 1920, 632A.

[117] *J. Franklin Inst.*, 1919, **188**, 675; *J.*, 1920, 15R, 34A.

L. Bock[120] points out the connexion between the colour of lead chromate pigments and their degree of dispersity. J. Scott[121] from a study of photomicrographs of lead carbonate in its various stages of precipitation from lead solutions and sodium carbonate, concludes that the spaces between the granules of lead carbonate are occupied by nuclei of lead hydroxide.

E. Euston[122] considers the porcelain-like crust formed in the stack process of making white lead to be caused by the cementing effect of the colloidal basic lead acetate present.

L. Bock[123] discusses the constitution of various ultramarines and shows evidence of their relationship to the zeolites. The preparation and chemistry of satin-white is dealt with by A. Cobenzl.[124] E. Euston[125] has patented a precipitation process for the manufacture of white lead, designed to yield a product of definite carbonate content. J. E. Seeley[126] treats a stream of melted lead with ozonised air, water, and carbon dioxide to form a lead pigment. F. G. Kidd and Wilkinson, Heywood, and Clark, Ltd.[127] claim the method of preparing precipitated pigments by causing the solutions to react in the form of spray in the presence of inactive or reactive gas. The Berlin-Anhaltische Maschinenbau A.-G.[128] have patented an apparatus for simultaneously producing lampblack and hydrogen. G. St. J. Perrott and R. Thiessen[129] publish a very full description of the commercial preparation and methods of testing carbon black.

W. Allsebrook[130] gives an account of the mono-azo dyestuffs for the production of coloured lakes and pigments regarded from the standpoint of the present English industry, whilst J. B. Shaw[131] deals with the process of the colour-striking of pigment lakes. W. R. Brass[132] patents the employment of the ammonium sulphite compounds of mono-azo dyes as intermediates in the preparation of pigment lakes.

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[118] *Cost Accounting Committee, Paint Manufrs. Assoc. U.S., Circ.* 104; *J.*, 1920, 356R.

[119] *Circ.* 85, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 306A.

[120] *Farben-Zeit.*, 1920, **25**, 761; *J.*, 1920, 341A.

[121] *Chem. Trade J.*, 1919, **65**, 327; *J.*, 1919, [illegible]

[122] *J. Ind. Eng. Chem.*, 1920, **12**, 974; *J.*, 1920, 756A.

[123] *Z. angew. Chem.*, 1920, **24**, 23; *J.*, 1920, 306A.

[124] *Chem.-Zeit.*, 1920, **44**, 661; *J.*, 1920, 664A.

[125] U.S.P. 1,349,334; *J.*, 1920, 664A.

[126] U.S.P. 1,325,960; *J.*, 1920, 164A.

[127] E.P. 134,313; *J.*, 1919, 954A.

[128] G.P. 312,546; *J.*, 1920, 664A.

[129] *J. Ind. Eng. Chem.*, 1920, **12**, 324; *J.*, 1920, 377A.

[130] *Proc. Oil and Colour Chemists' Assoc.*, II., 1919, 14, 126.

S. F. Grove[133] records an attempt to produce from sodium ferrocyanide Prussian blues equal to those made from the potash salt, by precipitating in the presence of potassium and ammonium salts and thereby effecting a considerable economy of potash salt.

A further number of processes dealing with the manufacture of composite pigments have been patented,[134] most of them comprising the use of titanic oxide. The use of the latter class of pigment appears now to have been definitely established, a variety having been placed on the English market. The writer understands that the non-reactivity and high opacity of such pigments have been found to be highly satisfactory in practice.

The use of specially-prepared antimony oxide as a pigment, although primarily a war-measure during the shortage of the more well-known pigments, has been maintained and a variety known as "Timonox" is finding an extended use in the paint and linoleum trades on account of certain special properties it possesses. A. L. Barbe[135] patents a process for converting antimony oxide into a pigment.

P. Chaillaux[136] patents a method of manufacturing antimony vermilion. A. Eibner[137] frees zinc solutions (for use in the manufacture of lithopone) from metals forming coloured sulphides and claims thereby to inhibit the photogenetic properties of the pigment.

PAINTS.

A. Molteni,[138] in dealing with the corrosion of iron and its prevention, summarises the experiences of results with so-called rust-inhibiting pigments in paints, whilst A. de Waele,[139] in a paper referred to in an earlier report, draws attention to the connexion existing between such property and specific oil absorption.

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[131] *Proc. Oil and Colour Chemists' Assoc.*, III., 1920, 17, 57.

[132] E.P. 134,270; *J.*, 1919, 943A.

[133] *Drugs, Oils, and Paints*, April, 1919.

[134] P. Desachy, F.P. 126,628; *J.*, 1919, 915A; A. P. Jaeger, U.S.P. 1,317,164 and 1,317,165; *J.*, 1919, 915A; Titan Co. A. S., G.P. 312,090; *J.*, 1919, 915A; V. M. Goldschmidt, U.S.P. 1,343,446, 1,348,129 and 1,343,447; *J.*, 1920, 552A, 633A; R. Nielsen and V. M. Goldschmidt, U.S.P. 1,343,468 and 1,343,469; *J.*, 1920, 552A.

[135] E.P. 140,301; *J.*, 1920, 377A.

[136] E.P. 151,422; *J.*, 1920, 756A.

[137] G.P. 324,646; *J.*, 1920, 757A.

[138] *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., 9, 25.

[139] *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., 13, 107.

The latter writer, in another paper[140] dealing with a method of costing ready-mixed paint from laboratory data only, claims that the viscosity of paint is a function of its volume relationship to that of its parent paste obtained from the preliminary grinding.[119] H. A. Gardner[141] refers to the corrosion of aluminium by weathering and the similar effect produced by application of basic pigments in presence of water, thus suggesting the employment of the latter system in the form of a paint to produce a " key " in priming coats. The same author[142] finds a similar action to apply to galvanised iron, and thereby suggests the inhibition of peeling in priming coats on galvanised iron by the use of a priming paint consisting of similar materials. In another paper[143] H. A. Gardner determines the illuminating power of various paints and finds that greater reflecting power is obtained from flat paints than from those with a glossy finish. An additional paper[144] deals with the spreading rates of prepared paint products on various surfaces.

H. P. Fletcher[145] claims the addition of a very small amount of manganese borate to assist in separation of water in the " wet-pugging " of pigments. The process is interesting in suggesting the influence of manganese borate in raising the interfacial tension of the pigment/water phase relatively to that of pigment/oil. The employment of naphthenic acid salts of mercury etc. is patented by H. Burstin[146] for use in ships' bottom paints.

PHYSICAL.

In addition to the developments in knowledge of the phenomena connected with the manufacture or application of the products of the paint and varnish industry dealt with under the separate headings, some further interesting work has been published, the application of which may also fall outside of the actual field of this section. In this respect one of the series of papers by E. C. Bingham and H. Green entitled " Paint; a plastic material and not a viscous liquid " is of especial interest, the experiments covered by the paper in question relating to paints in particular but forming obviously a basis of investigation for other systems. This paper[147] forms one of the most interesting and useful contributions to the practice of scientific paint technology of the year and has already led to the application of the principle involved by other investigators in their work. These writers have recognised paints to be plastic solids in contradistinction to viscous liquids, and their viscosities or rather "rigidities" to be in consequence subject to interpretation by a modification of Poiseuille's formula in which the term "yield value" occurs as f in the equation

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[140] *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., **13**, 115; *J.*, 1919, 195R.

[141] *Circ.* 79, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 116A.

[142] *Circ.* 80, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 121A.

[143] *Circ.* 76, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 72A.

[144] H. A. Gardner, *Circ.* 71, *Paint Manufrs. Assoc. U.S.*; *J.*, 1919, 953A.

[145] E.P. 122,612; *J.*, 1919, 187A.

[146] G.P. 319,199; *J.*, 1920, 665A.

[147] *Proc. Amer. Soc. Testing Mat.*, 1919, **19**, 640; *J.*, 1920, 292R, 495A.

$$\eta = KV/(P-f)$$

η being the mobility, or inverse of the rigidity. The yield value, then, is interpreted as the pressure requisite before movement through a capillary can take place, and is determinable from a series of figures obtained at varying pressures. In practice, "yield value" in paints will be found to manifest itself as the "shortness," a property quite distinguishable from viscosity. From actual results obtained by the authors, zinc oxide paint was found to show a low yield value in comparison with lead pigments, a result fully borne out in practice in its lesser "shortness" or improved "flow." Two striking instances of materials of high "yield values" and only moderate viscosities are, in the present writer's opinion, to be found in petroleum jelly and soap froths.

A. E Bawtree[148] independently devised a simpler form of viscometer applicable to the study of plastic systems such as paints but did not appreciate the factor of "yield value" in the results obtained. This was pointed out in the discussion following the paper[149] and the author's results when interpreted by the modified Poiseuille's equation showed interesting examples of yield values in several of the products examined. A curious point was shown in the examination of glycerin in the viscometer, losses in viscosity being registered with succeeding determinations, thus confirming the nature of glycerin as a solid existing at ordinary temperatures in superfused form.

Arising directly from the publication of Bingham and Green's work, G. St. J. Perrott and R. Thiessen,[129] in a paper on the properties of carbon black, examined the viscosities of linseed oil suspensions of "long" and "short" carbon blacks in a torsion viscometer. Although the mobilities of the two suspensions were found to be very similar, the "shortness" of one pigment was attended by a higher yield value than that found in the case of a "long" pigment. "Shortness" and high yield value of carbon black in an oil medium were found to be explicable by the agglomeration of individual particles of the pigment to aggregates, those varieties containing a higher proportion of volatile matter remaining dispersed, probably by reason of the layer of adsorbed matter acting as a protective film against aggregation.

O. Faust[150] finds that in the determination of the viscosities of liquids by the method of noting the time taken by an air bubble to rise through a measured vertical column of liquid, the use of a tube of 24–18 mm. diameter ensures correct results, as the time noted is then independent of the size of the bubble or the diameter of the tube. This point is of interest in view of the common use of such method by varnish makers in determining "body."

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[148] *Proc. Oil and Colour Chemists' Assoc.*, 1920, III., **16**, 109.

[149] *Ibid.*, 125-130.

[150] *Z. physik. Chem.*, 1919, **93**, 758 ; *J.*, 1920, 282A.

W. Ostwald[151] publishes a system of a scientific classification of colours, and A. Wirth[152] describes an apparatus for determination of the white, black, and coloured constituents in pigments according to this system. J. Lawrance[153] places colours in a geometrical colour solid and obtains colour matches with a rotating disc and tri-colour sectors. A. E. Bawtree[154] in criticising methods of colour-matching and registration depending on the obtainment of colour by subtractive effect, *e.g.* disc, tintometer, etc., describes an apparatus free from theoretical objection and depending on additive effect of the monochromatic colours of vision.

A turbidimeter for the examination of varnishes etc. has been described by S. E. Sheppard.[155]

Miscellaneous Analytical Methods.

H. Salvaterra[156] determines the saponification values of resins by a method involving precipitation of the soap with barium chloride and thereby probably facilitates this determination on dark-coloured products. H. A. Gardner and R. E. Coleman[157] employ a mixture of benzol and alcohol as solvents in the determination of acid values of varnishes and boiled oils, in order to convert colloidally-dispersed into molecular solutions and thus ensure true values being obtained.

M. Aida[158] detects minute quantities of petroleum spirit in vegetable oils by a method which involves an application of the formolite reaction. G. Chavanne and L. J. Simon[159] determine the proportion of aromatic and of saturated cyclic hydrocarbons in petroleum spirit by means of the critical temperature of solution in aniline. A. Allina and H. Salvaterra[160] deal with the determination of petroleum spirit in turpentine. L. M. Proctor[161] publishes comparative tests of the melting-

[151] *Chem.-Zeit.*, 1919, **43**, 681; *J.*, 1919, 914A.

[152] *Chem.-Zeit.*, 1920, **44**, 737; *J.*, 1920, 728A.

[153] *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., **6**, 1.

[154] *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., **11**, 61; *J.*, 1920, 430A.

[155] *J. Ind. Eng. Chem.*, 1920, **12**, 167; *J.*, 1920, 282A.

[156] *Chem.-Zeit.*, 1919, **43**, 765; *J.*, 1920, 72A.

[157] *Circ.* 87, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 306A.

[158] *J.*, 1920, 152T.

[159] *Comptes rend.*, 1919, **169**, 70; *J.*, 1919, 619A.

[160] *Chem.-Zeit.*, 1920, **44**, 673, 697; *J.*, 1920, 697A.

[161] *Chem. and Met. Eng.*, 1919, **21**, 81; *J.*, 1919, 619A.

point of asphalts by different methods. J. Tausz and A. Lüttgen[162] publish a rapid method for the determination of hard asphalt. D. F. Twiss and E. A. Murphy[163] describe an apparatus for determination of the softening-point of asphalts and other plastics, whilst E. C. Pailler[164] gives a method for distinguishing between natural and artificial asphalts.

L. McMaster and A. E. Goldstein[165] deal with a modification of the Thompson method for the determination of acetic acid in white lead; J. Milbauer and I. Setlik[166] separate lead for the analysis of chrome yellow etc. by electrolysis, whilst M. Gröger[167] determines chromic acid in this pigment iodometrically.

S. Stewart[168] employs the microscope as a means of detecting natural barytes in lithopone; the present writer would point out that such a test is carried out more conveniently by examination in polarised light.

H. H. Morgan[169] determines the "actually-free" sulphur in ultramarines by ether-extraction, giving results of a number of determinations, but does not suggest that such sulphur is alone responsible for undesirable qualities in certain samples of this pigment.

T. L. Crossley[170] publishes a rapid method for the examination of shellac varnish, but the present writer is not convinced that the process shows any advantage of rapidity or accuracy over that of McIlhiney.

An apparatus for carrying out the Browne heat test for tung oil has been standardised by H. A. Gardner[171] and adopted by the American Society for Testing Materials. P. E. Jameson[172] points to the retarding influence of free fatty acids in the polymerisation of tung oil in the Browne test, and removes free fatty acids by mixing the oil with calcium hydroxide and filtration previous to testing. The large amount of work published on the subject of the Browne test would suggest the desirability of general adoption of the standardised method, the writer's personal experience having confirmed the particular value of gelatinisation tests in the evaluation of tung oil. W. Devrient[173] from a consideration of the values found by the iodine absorption of elaidic acid from various iodine solutions, concludes that the Hanus solution yields results approaching more closely to theoretical values.

[162] *Chem. Zentr.*, 1919, **90**, IV., 25; *J.*, 1919, 754A.

[163] *J.*, 1919, 405T.

[164] *Caoutchouc et Gutta-Percha*, 1919, **16**, 10,063; *J.*, 1919, 940A.

[165] *J. Ind. Eng. Chem.*, 1920, **12**, 170; *J.*, 1920, 341A.

[166] *J. prakt. Chem.*, 1919, **99**, 85; *J.*, 1919, 646A.

[167] *Z. anorg. Chem.*, 1919, **108**, 267; *J.*, 1920, 34A.

[168] *J.*, 1920, 188T.

[169] *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., **13**, 120.

[170] *J. Ind. Eng. Chem.*, 1920, **12**, 778; *J.*, 1920, 632A.

[171] *Circs.* 84 and 100, *Paint Manufrs. Assoc. U.S.*; *J.*, 1920, 604A.

[172] *Analyst*, 1920, **45**, 328; *J.*, 1920, 697A.

[173] *Ber. deuts. pharm. Ges.*, 1920, **30**, 361; *J.*, 1920, 755A.

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INDIA-RUBBER.

By Henry P. Stevens, M.A., Ph.D., F.I.C.,

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There is nothing of outstanding importance to record in the literature on rubber during the current year, although further progress has been made in a number of directions indicated by previous work. The discovery of a new vulcanising process by S. J. Peachey, referred to in the last report, has attracted a good deal of attention. The process is admittedly novel. The reaction which takes place according to Peachey, viz. $2H_2S + SO_2 = 2H_2O + 3S$, is the well known one to be found in every text book. H. Skellon[1] however, suggests that the reaction is in fact more complicated, only part of the sulphur being liberated as such, the remainder forming pentathionic acid thus, $4SO_2 + 3H_2S = H_2S_5O_6 + 2S + 2H_2O$. The pentathionic acid slowly decomposes, liberating sulphur, sulphuric acid, and sulphur dioxide; the latter reacts again with more hydrogen sulphide, and so on. The end result is therefore that a small quantity of sulphuric acid is formed in addition to the water and sulphur. No proof, however, is given to show that sulphuric acid was actually formed. Peachey states that under normal conditions practically the whole of the liberated sulphur combines with the rubber and the product contains but a mere trace of free sulphur; the amount, however, depends on the skill with which the process is carried out. This matter of free sulphur has been raised several times, but the presence of a very limited amount is unlikely to be a matter of much importance, as all rubber vulcanised with sulphur contains more or less free sulphur. It is, however, interesting to learn that the presence of free sulphur such as that introduced by compounding with antimony sulphide and ultramarine is disadvantageous.[2] Possibly the free sulphur forms a nucleus on which the atomic sulphur is deposited so that the sulphur produced in the reaction is liberated as free sulphur instead of combining with the rubber. There

[1] *Rubber Age*, Dec., 1920, 443.

[2] S. J. Peachey, *J.*, 1921, 5T.

may be a limit to the thickness of rubber which can be effectively vulcanised, but the incorporation of fillers favours the penetration of the gases. According to H. L. Terry,[3] the vulcanised product more closely resembles a hot-cured than a cold-cured rubber, and is not easily reclaimed like the latter.

Of publications other than contributions to the scientific and technical journals, special reference must be made to G. S. Whitby's recently published book, "Plantation Rubber and the Testing of Rubber,"[4] which deals very fully and in a scholarly manner with the scientific and technical aspects of these subjects. It is the most comprehensive and exhaustive work on rubber research so far published, and contains a very complete bibliography.

STATISTICS.

The output of plantation rubber continues to increase and represents 89·5% of the total world's production. As in the past, the production of wild rubber, mainly Brazilian, shows little change. The output has now got ahead of consumption; an excess of 50,000 tons for the year is anticipated, with a result that at the time of writing the price of plantation rubber has fallen to a lower figure than ever before and is in fact appreciably below the cost of production. This position is generally attributed to the falling off in demand from the United States and Canada, countries which normally consume two thirds to three quarters of the world's output, and also to the inability of Continental countries to purchase even at the present low price on account of the adverse exchanges. The estimated output[5] of plantation rubber for the present year is 343,000[6] tons, the corresponding figures for 1919 being 302,000 tons. In the last seven years the output has quadrupled.

PRODUCTION OF RAW RUBBER.

O. de Vries and his colleagues have continued the publication of papers dealing systematically with the factors in coagulation affecting the properties of vulcanisation. Work in this direction is confined to these reports and communications by the writer in the *Bulletin of the Rubber Growers' Association*. An account of de Vries' work on the specific gravity of latex was given in the last report[7] which tended to show that the Metrolac or other form of hydrometer was not a suitable instrument for the purpose of ascertaining the dry rubber content of the latex. This conclusion was based on theoretical considerations and on the results of actual tests. It is curious, however, that the scale of the Metrolac agrees fairly closely with B. J. Eaton's scale which was worked out independently, and it would appear that the Metrolac scale holds good for the average bulked latex in Ceylon and the F.M.S. It is in fact based on the average latex. Figures are given in a recent paper[8] showing the results obtained on an estate where the Metrolac was regularly employed for estimating the rubber content of the latex. From this and the volume of the latex the yield of rubber was calculated and found at the end of the year to differ only by about 1% from the amount of the crop actually secured. It is, however, admitted that the rubber content of individual samples of latex can only be very roughly estimated by a determination of the specific gravity. The causes of this discrepancy require further investigation, but it is known that abnormal figures are given by latex from trees when first tapped and by diseased trees. It is possible that this abnormality may be found to give warning of the presence of disease before other symptoms make their appearance.

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[3] *Rubber Age.*, Dec., 1920, 443.

[4] Published by Longmans, Green & Co. See also a review by the writer of this report in *Nature.*

[5] *Bull. Rubber Growers' Assoc.*, 2, 6, 362.

[6] The Rubber Growers' Association Restriction Scheme for a 25% reduction in output came into force at the beginning of November. This was adopted by the great majority of producers and will reduce the estimated output for 1920.

More attention is now being directed to (1) seed selection and the propagation by other means of the best strain of trees, *i.e.*, those giving the largest yields and showing the greatest resistance to disease, and (2) the selection of trees for thinning out. The latter is the more pressing problem. It is now admitted that thinning out is essential after a certain period of growth in order to give room for development, as practically all areas carry too many trees per acre for a permanent plantation. When planting up an allowance must be made for losses during growth, and consequently in most cases it will be necessary to plant more trees than the land can eventually carry. Diseased trees can be removed without compunction. Of the remainder some consideration must be paid to spacing, otherwise regard should be had to rubber-yielding capacity. The yields of individual trees varies very greatly. G. S. Whitby[9] was the first to publish figures showing the extent of variation. A small proportion of trees gave relatively very high yields—up to five and six times the average—so there appears to be ample scope for selection. The actual yields varied from 1 to 43 g. and the rubber content of the latex from 23% to 55%. More recently de Vries[10] has published figures showing a variation in yield from 4 to 71 g., and the rubber content of the latex from 17% to 50%. These figures are of the same order as Whitby's and fully confirm the variation noted. To utilise such variations it must be shown that yields are substantially constant over long periods, *i.e.*, good "milkers" can be relied upon to continue so. There are very few published figures, and the results of measurements given are generally over short periods. The evidence so far available[11] points to consistency in yields of individual trees. A systematic investigation is desirable. There are several other differences noted in the latex of individual trees such as colour, tendency to coagulate, surface darkening of the clot, viscosity of the rubber produced, and rate of cure. All these properties fluctuate and some individual trees yield abnormal latex. Other methods of selecting trees can only be cited here. There is the propagation from cuttings or grafts of trees known to be good yielders or, in the case of ordinary seedlings, a microscopical examination of the cortex may be made before planting out to ascertain the number of layers of latex vessels.

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[7] *Ann. Repts.*, 1919, 4, 318.

[8] H. P. Stevens, *Bull. Rubber Growers. Assoc.*, 1919, **1**, 44, 45.

[9] *Ann. Repts.*, 1919, **4**, 313.

[10] *Archief voor de Rubbercultur*, 1920, **4**, 268 ; *J.*, 1920, 665A.

Some systematic work has been carried out on latex coagulation. O. de Vries and W. Spoon[12] find that rubber coagulated spontaneously in the absence of air is indistinguishable in vulcanising properties from that coagulated with acetic acid. Spontaneous coagulation is partial and therefore unsatisfactory with latex from heavily tapped trees and with that collected in July and August when the trees are wintering. It is rapid and complete when the latex is of high rubber content such as that yielded by trees which have been resting. Spoon[13] finds that satisfactory coagulation can be obtained by the addition of 0·1% of calcium chloride. Both these observations are confirmatory of earlier work showing the favourable effect of calcium salts on coagulation.[14]

Arisz[15] has studied the influence of heavy tapping on the composition of the latex, and from the analytical data concludes that the percentage of resin (acetone extract) remains constant, but that after the first fortnight the organic matter in the serum decreases. This applies also to the nitrogenous constituents both in the latex and serum. On the other hand the percentage of inorganic constituents is not affected by heavy tapping. O. de Vries has also contributed a paper on the same subject.[16] Heavier tapping, whether obtained by increasing the length of the tapping cuts, increasing the number of cuts, or making deeper incisions down to the wood itself, produces a similar effect, namely, decrease in rubber content with a corresponding increase in the specific gravity of the latex and a faster vulcanising rubber. Latex and rubber of practically identical composition were obtained from cuts at different heights on the tree. Tapping earlier in the day gave a latex of rather lower rubber content than that obtained by tapping later, but the properties of the rubber showed no alteration.

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[11] *Bull. Dept. of Agriculture Ceylon*, 4, 13.

[12] *Archief*, 1920, **4**, 308; *J.*, 1920, 665A.

[13] *Archief*, 1920, **4**, 331; *J.*, 1920, 665A.

[14] *J.*, 1917, 274.

[15] *Archief*, 1920, **4**, 30.

[16] *Archief*, 1920, **4**, 331.

O. de Vries[17] confirms the retarding effect caused by soaking fresh coagulum in water—no doubt due to leaching out of constituents of the serum, as the change is accompanied by loss of weight. Long soaking causes an increase in rate of cure so that the original retardation is converted into an acceleration, presumably caused by putrefaction setting in. H. P. Stevens[18] has studied the effect of soaking in water and acids such as acetic or sulphuric acid. The accelerating effect of long soaking was not noted, but this was no doubt due to changing the water every day or two. The retarding effect increases with the concentration of the acid, and is greater with sulphuric acid than with acetic acid. In fact the effect of soaking in these acids is similar to that of their use for coagulation. Subsequent experiments with the rubber showed that re-soaking in water tended to restore the rate of cure and the conclusion was reached that the retardation caused by acids is only partly to be accounted for by a leaching out of serum substance, but largely through retention of traces of acid by the rubber. De Vries[19] has also published results of tests on rubber coagulated with different reagents. With small proportions of sulphuric acid the rubber was comparable in properties with that coagulated with acetic acid, whereas Stevens found that even the minimal proportion of sulphuric acid gave a much slower curing rubber than a similar proportion of acetic acid. Both de Vries and Stevens[20] confirm the slow curing properties of alum; the latter, however, finds that much depends on whether the proportion of alum used is the minimum or not. The slight excess necessary to produce a "clean coagulation" with clear serum causes a considerable increase in retardation. De Vries found a retardation amounting to about 15% as against minimal proportions of acetic acid and Stevens a retardation of 9%. With large proportions of alum a very considerable retardation is obtained, as would be expected. The retardation is, however, not greater than would be obtained with sulphuric acid and does not appear to justify the enactment forbidding the use of alum as a coagulant in the Federated Malay States when sulphuric acid and even less desirable coagulants are permissible. Alum-coagulated rubber shows no deterioration in keeping, but both investigators find that hydrochloric acid gives a rubber which tends to go tacky. The suitability of acetic acid as a coagulant is largely due to the very slight effect it exercises on rate of cure, and it has been stated that the proportion can be appreciably increased beyond the minimum without affecting the rubber. In a series of experiments Stevens[21] has determined the retardation caused by progressive increases in the proportion of acid used for crêpe, smoked sheet, and slab rubbers, plotting the results graphically. The retardation is least in the case of crêpe rubber, a tenfold proportion of acid producing only a 10% reduction in rate of cure. Smoked sheet is more sensitive, and the effect is two or three times as great as with crêpe. Crêpe from matured latex gives a much steeper curve, so that with a very large excess of acid a rubber is produced curing more slowly than either sheet or crêpe.

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[17] *Archief*, 1919, **3**, 369.

[18] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 343; *J.*, 1920, 826A.

[19] *Archief*, 1920, **4**, 210.

[20] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 142; *J.*, 1920, 826A.

Little or no progress appears to have been made with the prevention of mould growths on sheet rubber, although a number of antiseptics have been tried at different times. Mouldy sheets are said to cure more slowly and the rubber may be of inferior quality. Such statements are difficult of proof or disproof as suitable control sheets for comparison with the mouldy ones are not available. The majority of mouldy sheets are not badly affected, and in the writer's experience they are not appreciably slower curing or of an inferior quality. The tests were made by cutting out the mouldy parts from a few sheets and comparing the quality with the sound parts. It was noted that sheets partially covered with mould were after washing more opaque in the parts where the mould growth had occurred. An apparently exactly similar darkening of smoked sheets in patches has been noted by J. C. Hartjens.[22] These markings are not visible on sheets until after one or two days' smoking. Various factors in preparation, with the exception of an excess of sulphite or bisulphite, had no influence on the tendency to form these dark patches. The author does not appear to have connected the dark patches with mould growths.

Some years ago "chinosol" was introduced for the prevention of the coloured spots which appear in crêpe rubber but not in smoked sheet. These are attributed to microscopic fungi. Presumably smoking is a sufficiently antiseptic treatment to prevent their growth. The present writer found that almost any crêpe rubber, including vacuum-dried block, will develop spots if incubated in a moist atmosphere, but the presence of a piece of smoked sheet in the same receptacle with the crêpe will prevent the latter from developing spots. The ordinary surface moulds are much more resistant, as neither chinosol[23] nor thorough smoking will prevent their appearance. There is no doubt, however, that smoking has a distinctly inhibitive action, for smoked sheets are much less liable to mould than unsmoked sheets. The market objection to an " over-smoked " sheet has caused estates to smoke lightly, and this may possibly account for the complaints made as to the greater prevalence of mouldy sheets at the present time.

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[21] *Bull. Rubber Growers' Assoc.*, 1919, **1**, 39; *J.*, 1920, 199A.

[22] *Archief*, 1920, **4**, 159.

When latex coagulates spontaneously or is allowed to mature in air, the effect of the atmospheric oxygen is apparent from the difference in the changes (A) on the surface; (B) in the interior of the coagulum. The former is alkaline, the latter acid. Eaton, who made exhaustive studies on maturation, obtained inconclusive results as to the rate of cure of rubber prepared under aërobic and anaërobic conditions. Stevens has carried out further experiments[24] comparing the rate of cure of internal and external parts from the same mass of coagulum without finding much difference in properties. The rubber was prepared in crêpe form from the matured coagulum, for Eaton showed that crêpe in spite of treatment on the washing rollers retains its rapid curing properties. Nevertheless, the soft alkaline slime from the surface would be very completely washed away. Similar negative results were obtained with rubber spontaneously coagulated in closed and open vessels. A considerable difference was, however, noted in the case of sheets of different thicknesses allowed to mature for a week, then dried and tested.[25] It was found that the rate of cure fell as the thickness of the sheets increased until a sheet of about ordinary thickness was reached. A still thicker sheet or " slab " gave a greater rate of cure, although not equal to that of the thinnest sheet. It therefore appears that the area of exposed surface does influence the vulcanising properties in the direction one would expect, that is to say, by increasing the rate of cure, but that other factors come into play when the thickness of the sheet is increased beyond the usual limits.

A series of comparative tests on crêpe from freshly coagulated rubber and matured coagulum[26] showed that the latter exhibited much greater variation in rate of cure than the former. This has a bearing on the utilisation of rubber from such matured coagulum for manufacturing purposes as advocated in some quarters. It has been shown that keeping latex a few hours longer previous to coagulation (as is sometimes unavoidable in estate working) has but little effect on rate of cure; at the most a slight accelerating effect is produced. Occasionally latex tends to clot almost immediately it flows from the tree; this effect is climatic rather than specific for individual trees, and is often observed if the bark surface is wet when tapping takes place after overnight rain. Presumably some coagulant, possibly of the nature of tannin, contaminates the latex. This viscous latex when converted into rubber cures appreciably faster than latex from the same trees showing normal consistency.[27]

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[23] W. Spoon, *Archief*, 1920, **4**, 344.

[24] *Bull. Rubber Growers' Assoc.*, 1919, **1**, 42; *J.*, 1920, 199A.

[25] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 212; *J.*, 1920, 826A.

[26] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 68, *J.*, 1920, 198A.

It has been frequently stated that fine hard Para is more uniform than plantation rubber, which is probably true if the comparison is made with all types and grades of plantation B. J. Eaton, however, published figures[28] to show that fine hard Para varied less in rate of cure than one type of plantation such as "first latex" crêpe or sheet. Stevens has repeated these tests[29] but with different results. The samples of fine hard Para showed as great or greater variation than a series of pale crêpe rubbers. This conclusion was based on his own figures of variation in plantation rubber and also on those of de Vries, which are of the same order. It is probable that Eaton's samples were not taken from individual balls of fine hard Para but that each sample consisted of several pieces cut from different balls. This would explain the uniformity of Eaton's figures.

VULCANISATION.

C. W. Sanderson[30] has studied the behaviour of rubber during vulcanisation by measuring the change in volume. He found that the higher the rubber content the greater the expansion, and the harder the crude rubber the less the expansion. Milling also increases the expansion. The changes are gradual throughout and there are no breaks in the curves.

ACCELERATORS.

Several papers have been published on this subject. G. D. Kratz and A. H. Flower continue the work summarised in the last report[31] and have again taken up the study of magnesia as an accelerator particularly in reference to the present writer's comparative tests of the efficiency of this substance as compared with organic accelerators.[32] It will be remembered that magnesia proved particularly effective when used in very small quantities—up to about 0·5%. Kratz and Flower suggest[33] that the action of magnesia is an indirect one and that its function is to activate the "extraneous substances (probably nitrogenous)" naturally present in the rubber. This would account for the limited effect obtainable with magnesia of which only very small quantities are required to activate the natural accelerator. On the assumption that the extraneous substance is soluble in acetone, Kratz and Flower made comparative tests with an acetone-extracted rubber and an unextracted control. In the former 0·5% of magnesia produced far less acceleration than in an unextracted control. On the other hand the addition of 0·5% of an organic accelerator produced practically the same accelerating effect in the extracted rubber as in the control. The authors refer to the reduction in rate of vulcanisation produced by acetone extraction, which they attribute to the removal of the acetone-soluble nitrogenous constituent. The figures given by them, however, do not confirm this assumption, in that prolonged acetone extraction in one case did not reduce the rate of vulcanisation, while in the other it was actually increased by about 50%. The experiment appears to indicate that the constituent activated by the magnesia is soluble in acetone, but it does not appear to be identical with the natural accelerator, which is not readily washed out and cannot be extracted with acetone, or at any rate cannot be reduced by acetone extraction below a certain limit. A closer investigation of the nitrogenous constituents naturally present in rubber is necessary before these points can be correctly interpreted.

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[27] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 214; *J.*, 1920, 826A.

[28] *Bull. Dept. Agric. F.M.S.*, **27**, 364.

[29] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 347; *J.*, 1920, 826A.

[30] *J. Ind. Eng. Chem.*, 1920, **12**, 37; *J.*, 1920, 199A.

[31] *Ann. Repts.*, 1919, **4**, 330.

[32] H. P. Stevens, *India-Rubber J*, 1919, **58**, 527; *J.*, 1918, 156T.

[33] *J. Ind. Eng. Chem.*, 1920, **12**, 971; *J.*, 1920, 757A.

The activating properties attributed to magnesia by Kratz and Flower have a parallel in the case of zinc oxide and litharge. The effect of zinc oxide was first demonstrated by D. F. Cranor.[34] In his experiments with accelerators he added one part of zinc oxide with 6 parts of sulphur to 100 parts of raw rubber. Without the addition of an organic accelerator he found that the optimal physical properties could not be taken as vulcanisation criteria because specimens so vulcanised were obviously overcured. Basing his conclusions on an accelerated ageing test, he found that the best cured specimen had a coefficient of 2·85, which corresponds satisfactorily with the figure obtained by other investigators.[35] When, however, an accelerator was added (hexamethylenetetramine or dimethylammonium dithiocarbamate), the best cured specimens, *i.e.*, from the tensile and ageing point of view, were those giving an appreciably lower coefficient, many figures being as low as one unit. In a series of ageing tests with a mixture without accelerators, but containing a considerable amount of zinc oxide and 5% of sulphur calculated on the rubber, Stevens[36] has recently shown that a coefficient of 2 units was approximately the maximum giving satisfactory ageing figures. The course of ageing is similar in both types of mixing as shown by the curves.

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[34] *India-Rubber J.*, 1919, **58**, 1201; *J.*, 1920, 73A.

[35] Stevens, Spence, Kratz, van Heurn, and others.

[36] *Bull. Rubber Growers' Assoc.*, 1920, **2**, 270; *J.*, 1920, 826A.

D. F. Twiss and S. A. Brazier have supplied further evidence of the influence of zinc oxide on organic accelerators.[37] Thus thiocarbanilide of itself is practically inert as an accelerator, but in the presence of 1% of zinc oxide a very appreciable acceleration is produced. Similarly the effect of hexamethylenetetramine is considerably enhanced by a similar addition of zinc oxide. A number of other interesting results are detailed by the same authors. It is pointed our that three methods are ordinarily available for accelerating vulcanisation: (1) raising the temperature, (2) increasing the proportion of sulphur relative to rubber, and (3) introducing an accelerator. The progress of vulcanisation in each case was studied by determining (A) the percentage of sulphur combined with the rubber, (B) the decrease of extensibility under a given load (or increase of load required to produce a given extension), and (C) the time required to produce the maximal tensile strength. In experimental work (2) is usually constant—about 10% on the rubber. An increase in the proportion of accelerator produces a series of curves which generally resemble those obtained by raising the temperature. Accelerators, however, differ not only in general efficiency but specifically. With some the physical effect produced is disproportionally rapid as compared with the rate of combination with sulphur, and the maximal tensile strength is reached with a coefficient appreciably lower than is usual with rubber compounded with sulphur alone. This observation is in agreement with Cranor's figures. By tracing the results graphically the specific characteristics of these accelerators become apparent. Thus some reduce the sharpness of the peak so that the decrease in tensile strength beyond the maximal figure is less pronounced. In other cases the authors find that abnormality is displayed in the extensibility rather than in the tensile strength, and in general the addition of most, if not all, accelerators produces higher maximal figures owing to the reduction in the time or temperature of heating such as may also be obtained by increasing the proportion of sulphur. It is apparent therefore that the choice of an accelerator should not be confined merely to the required acceleration of vulcanisation, but should be extended to the physical properties it is desired to influence. Working with aldehyde-ammonia—a powerful accelerator—it was found that the temperature coefficient through a range of temperatures from 108° to 140° C. bears a practically constant ratio to that of the same mixing without the accelerator, and that very similar figures are obtained whatever the method of testing, *i.e.*, whether chemical or physical. In a subsequent paper D. F. Twiss and C. W. H.

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[37] *J.*, 1920, 125T.

Howson[38] call attention to some further abnormalities in the action of accelerators in the presence of zinc oxide. There is a curious break in the curves of vulcanised compounds containing this substance and hexamethylenetetramine or triphenylguanidine. Thus with the former maximal tensile and elongation figures are obtained with a coefficient of 4–5, which represents about the usual figure; this is followed by a sharp drop in values as ordinarily noted, but on prolonging the vulcanisation the figures show a secondary improvement although they do not reach such high figures as obtained in the earlier maxima. These observations have no practical value as far as the present examples are concerned, as the secondary maxima are only obtained under conditions at which the specimens are grossly overcured. It is, however, conceivable that under some conditions both maxima may lie within the limits of a technically cured rubber.

Of other work bearing on accelerators mention may be made of the paper by C. W. Bedford and W. Scott[39] dealing with the reactions taking place between organic accelerators and sulphur during vulcanisation; also the suggested use of the colour bases of basic coal tar dyes as accelerators.[40] In addition to the acceleration produced it is claimed that in some instances the rubber becomes coloured throughout the mass.

Apart from vulcanisation there is nothing to report as regards other reactions of raw rubber with the exception of two papers dealing with the bromine addition product. This reaction has been studied in great detail in the past with a view to adapting the product—a tetrabromide—to analytical purposes. G. Hübener,[41] who has published several papers on the subject, finds that synthetic "methyl-rubber" gives a bromide with a higher proportion of bromine than the natural product. W. C. Schmitz[42] has studied the bromination of natural rubber after "depolymerisation," that is to say, after heating rubber "dissolved" in an inert solvent at a relatively high temperature for a long period. It is well known that under these conditions a "solution" of rubber is obtained with very low viscosity, the rubber being markedly degraded. It was found that the bromine consumption of rubber so treated was greater than required for the formation of a tetrabromide and in the proportion of $5Br : C_{10}H_{16}$. The product readily splits off 2HBr, yielding a microcrystalline substance $C_{20}H_{30}Br_8$. The difference in behaviour of the raw rubber before and after "depolymerisation" is ascribed to the state of aggregation or molecular complexity.

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[38] *J.*, 1920, 287T.

[39] *J. Ind. Eng. Chem.*, 1920, **12**, 31; *J.*, 1920, 199A.

[40] L. Gaisman and J. L. Rosenbaum, E.P. 141,412; *J.*, 1920, 460A.

[41] *Gummi-Zeit.*, 1919, **32**, 361; *J.*. 1920, 307A.

[42] *Gummi-Zeit.*, 1919. **34**, 167; *J.*, 1920, 73A.

It may be remarked that in such cases it is impossible to supply any proof that the molecule is actually broken down to a simpler complex of the same percentage composition. It appears to be generally assumed that a loss in tensile properties of the raw rubber or a fall in the viscosity of the solution in an inert solvent is a sufficient proof of depolymerisation, but as nothing is known of the size of the caoutchouc molecule before and after such " depolymerisation " the assumption does not appear to be justified. If it be taken as proven that caoutchouc after prolonged heating in a solvent combines with a larger proportion of bromine, this may point to decomposition rather than depolymerisation in the ordinarily accepted chemical sense. In the present state of our knowledge it appears useless to speculate without further investigation. The work of Schmitz is, however, of great interest and it would certainly appear worth while to study other caoutchouc reactions on these lines. So far as we know mechanical treatment of raw rubber does not influence the rate with which it combines with sulphur.

COMPOUNDING INGREDIENTS.

A reference was made in the last report[43] to the use of zinc oxide and carbon black as compounding ingredients and to a possible connexion between the size of the particle and the specific effect of certain of these ingredients on the properties of the vulcanised rubber. Two papers have been published on this subject.

Wiegand[44] has given a series of stress-strain curves for a standard mixing to which varying proportions of different inert mineral ingredients were added. The results are suggestive and in accordance with the prevailing views on the effect of inert minerals when used for loading rubber, namely, that their value in most instances is directly connected with their state of subdivision. A " basic mixing " was chosen containing litharge and a relatively small proportion of sulphur (5% on the raw rubber taken) "so balanced as to preserve a practically flat curing condition " over a considerable range or cure " to avoid the tedium of doing a whole series of cures for each mixing." To this mixing varying proportions of different inert mineral ingredients were added. For each mixing one cure only was made, presumably under the same conditions. It is doubtful how far the use of this " flat cure " mixing is justifiable and the method has already met with criticism. The results, so far as they go, indicate that the finer the state of subdivision the larger the proportion of inert filling which can be incorporated without loss of tensile strength, the rubber merely suffering reduction in elongation under a given

[43] *Ann. Repts.*, 1919, **4**, 324.

[44] *India-Rubber J.*, 1920, 425.

load. The use of these finely divided minerals within limits (up to about 40% in the case of carbon black) enables the rubber to be hardened or stiffened without loss of tensile strength as measured on the original cross-sectional area of the test piece. If, however, the measurement were made on the cross-sectional area at the moment of rupture, the breaking strain would show a regular reduction as the proportion of pigment was increased. A table is given showing the relationship between the size of the pigment particles and the effect of the individual pigment. Presumably the measurements are approximate only as no details are given, but the results are sufficient to show that zinc oxide behaves differently to the other pigments, the effect produced being greater than would be anticipated from the size of the particle. It has been shown by H. F. Schippel[45] that compounded rubber under strain undergoes appreciable increase in volume; the larger the particles the greater the increase. The increase in volume in the case of zinc oxide is actually less than with any other of the pigments investigated although the particles are of intermediate size. The following table embodies the results for mixings containing 20 volumes of pigment.

Pigment.	Apparent surface.	Displacement of stress-strain curve.	Total energy of resilience.	Volume increase % at 200% elongation.
Carbon black	1,905,000	42	640	1·46
Lampblack	1,524,000	41	480	1·76
China clay	304,800	38	405	—
Red oxide	152,400	29	355	1·9
Zinc oxide	152,400	25	530	0·8
Glue	152,400	23	344	—
Whiting	60,900	17	410	4·6
Fossil flour	50,800	14	365	3·5
Barytes	30,480	8	360	13·3

The displacement of the stress-strain curve refers to the increase in load supported at a given elongation, that is the resistance to stretching. In respect to this property zinc oxide falls into place in accordance with the size of its particle. But as regards the total energy of resilience, which is based on the measurement of the area contained between the stress-strain and the elongation axis, zinc oxide takes up a position more nearly corresponding to the volume increase under strain.

The second paper on this subject, by C. O. North,[46] does not give the stress-strain curves but only the final figures for tensile strength, elongation, and permanent set. The mixings were composed of rubber, sulphur, and the compounding ingredients vulcanised in each case to give the "best cure at 40 lb. steam." No indication is given as to the meaning of "best cure" and the results are complicated in the case of two ingredients (barytes and zinc oxide) by the introduction of thiocarbanilide. To arrive at comparable figures the results were recalculated in terms of the rubber contained in the mixing irrespective of the nature of the mineral ingredient, whereby a considerable modification ensues. The data are too complicated to discuss in detail, but it may be said that the results obtained show the same tendency as in Wiegand's figures, gas black and zinc oxide showing up favourably while barytes functions as a diluent. In the latter case the tensile strength, corrected in the manner above described, was independent of the amount of filler. The results so far published are fragmentary and incomplete, but the subject is of such extraordinary importance to the manufacturer that we may confidently look forward to the publication of further data.

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[45] *Ann. Repts.*, 1919, **4**, 324.

[46] *India Rubber World*, 1920, **63**, 98.

Ageing of Raw and Vulcanised Rubber.

It is well known that light and oxygen promote changes in rubber which may be summed up under the term degradation; such changes take the form of tackiness and subsequent resinification in the case of raw rubber and a loss of tensile properties, hardness and subsequent perishing in the case of vulcanised rubber. Similarly changes take place when raw rubber is "dissolved" in organic solvents. These changes are apparent from a rapid reduction in viscosity particularly on exposure to light. The fall in viscosity is so rapid that repeat determinations always show lower figures unless carried out in semi-darkness. In a recent paper B. D. Porritt[47] shows that light may have the reverse effect on the viscosity of raw rubber sols if these be protected from the air in sealed tubes. Such sols rapidly gel on exposure to light but become fluid again on opening the tube and letting in the air. He also states that exposure to air in the absence of light does not reduce the viscosity. In the case of masticated rubber the viscosity tends to increase corresponding to a recovery in the physical properties of the rubber.

H. P. Stevens[48] has studied the ageing of vulcanised rubber when placed in an atmosphere of inert vapour. As is well known, perishing is accompanied with oxidation and the emission of acid vapours having a peculiar pungent odour and reducing properties. Inert vapours retard these changes. Petroleum (kerosene) was recommended long ago for this purpose.[49] The rubber takes up some of the vapour and swells; this gives it a soft and supple feel which may be deceptive. Nevertheless the rubber is preserved so long as it is immersed in petroleum vapours. Another method of preserving rubber goods is to immerse them in water. This is hardly applicable in many cases. No doubt the almost entire exclusion of oxygen explains the preservative effect of immersion. It is, however, now found that the amount of moisture in the atmosphere is the controlling factor (apart from manufacture) in the perishing of rubber goods. The moister the atmosphere the slower the deterioration, and in saturated air the change appears to take place as slowly as if the air were entirely excluded. An American firm[50] manufacturing zinc oxide have made a series of accelerating ageing tests on zinc oxide compared with carbon black stocks. The former was found to age far more satisfactorily than the latter, although there is some doubt how far the results were affected by the high percentage of hexamethylenetetramine employed as an accelerator in the compounds.

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[47] *Rubber Age*, 1920, 445.

[48] *J.*, 1920, 251T.

[49] Hempel, *Ber.*, **15**, 914.

THE STRESS-STRAIN CURVE.

Last year Schidrowitz in conjunction with Hatschek and Goldsbrough published further details of the method put forward by them some years ago for the interpretation of rubber stress-strain curves.[51] The conclusion was reached that these curves were conchoids, and the relationships were calculated on the basis of curves of this type. Particular emphasis was laid on the "slope" or type which embodies two of the three constants of the rubber under investigation. The "correct cure" was defined as that corresponding to a curve in which $a=b$, a being the distance between the pole of the curve and the asymptote and b the limit of extension, or in the words of the authors the condition in which "toughness or tenacity equals the limit of extension." It was found in practice to correspond to those cures judged to be correct by the "various empirical methods available."

These conclusions have been subjected to comment and criticism from two quarters, and although objection has been taken to certain of the authors' statements the verdict on the whole is favourable. W. B. Wiegand[52] reviews the physical researches on rubber[53] and brings into prominence the results to be derived from a study of the stress-strain curves when compared with a series of conchoids. He finds that the position of these curves can be duplicated in the case of the conchoid series by increasing or diminishing b, but the analogy fails when b is equal to or greater than a. He regards as inadequate the reasoning on which the author bases is conception of a perfect cure—that is the equivalence of a and b s an “ideal balance of properties.” He thinks, however, that he concordance of the figures for “perfect cures” with the “ortho-ox criteria of optimum tensile strength and optimum tensile product” should reconcile us to the views put forward. He con-ludes, however, by stating that “most of us will adhere to our present criteria rather than trust entirely the conchoid constants and b.”

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[50] De Pew in a paper read at a recent meeting of the American Chemical Society.

[51] See *Ann. Repts.*, 1919, **4**, 336, *et seq.*

[52] *Rubber Age and Tyre News*, 1920, 332, *et seq.*

[53] See also Part 2 of Whitby's "Plantation of Rubber and the Testing of Rubber."

Wiegand's paper is a general review of the subject, and he has ot considered it necessary to supply proofs or give references in upport of many of the statements made. Explanation is also equired of terms such as “optimum tensile strength.” Almost very worker on the problem of the evaluation of plantation rubber as a different opinion as to what constitutes the optimum con-ition of vulcanisation. When dealing with a mixing of fixed omposition the coefficient of vulcanisation cannot be ignored as he author suggests. A reference to some of the results recorded n this paper indicates that the relationship between the coefficient nd the tensile properties may well prove the key to some of the problems of vulcanisation.

O. de Vries[54] in a recent paper dealing with the stress-strain urve also refers in detail to Schidrowitz' proposals. He regards he stress-strain curve as S-shaped; consequently it cannot be epresented by a conchoid in which $a=b$. Schidrowitz has laid great stress on the parallelism of the almost straight portions f the curves just beyond the point of inflexion. This applies to a eries of curves corresponding to a series of cures at different emperatures. De Vries challenges the statement that the “straight ortions” of the curves are parallel, from which it follows that the nclination or “slope” is not independent of the state of cure. De Vries points to the reproductions of stress-strain curves of ifferent investigators, even of Schidrowitz himself,[55] and it must e admitted that the latter parts of the curves appear to be only pproximately parallel. The difference between these curves and he conchoids as illustrated in Wiegand's paper is also apparent. De Vries concludes that the stress-strain curves cannot be repre-ented by conchoids but that the relationship is a more complicated ne. The “slope” or resistance to stretching at the latter part f the curve is considered by de Vries as well worth attention as n independent property of the rubber apart from tensile strength nd rate of cure.

SYNTHETIC RUBBER.

Since the war a number of samples of the German synthetic products have been examined.[56] They appear to consist of the so-called methyl rubber, that is the polymerised product of dimethylbutadiene prepared by converting acetylene into acetone, thence into pinacone, which by loss of water is converted into dimethylbutadiene. Two types were produced, one by polymerisation over a long period at a relatively low temperature (mark H) and the other in a shorter period at a higher temperature (mark W). All synthetic products of this type show a great tendency to oxidation, and the properties of the products may be explained on the assumption that some oxygen has been absorbed. To stabilise the product various nitrogenous substances such as tolidene may be added. It is also necessary to incorporate plasticising ingredients, the so-called elasticators, in order that the rubber may be sufficiently plastic to work on the rollers. Synthetic rubber is usually met with as a thick crêpe, dark brown or red-brown and opaque (mark W). Acetone extracts most of the colouring matter, which is probably derived from stabilising, accelerating, or plasticising ingredients. This variety swells but only slowly dissolves in benzene after mastication. It breaks down on the hot mill and readily takes up mineral ingredients, but does not run very smoothly and is difficult to sheet. Synthetic rubber is also met with as a colourless and transparent mass. This type is harder and has a more leathery feel than mark W. It is even less "soluble" in the ordinary rubber solvents. Both types are tough but have not the resilience of natural rubber. When vulcanised the products are no better than obtainable with the inferior dark plantation crêpe.

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[54] *J.*, 1920, 308T.

[55] *J.*, 1919, 347T.

ANALYTICAL PROCESSES.

The importance of a rapid, reliable, and accurate method of estimating sulphur in vulcanised rubber has led to a further investigation of the oxidation methods by P. Dekker.[57] The method of Waters and Tuttle is preferred (oxidation with nitric acid and bromine and fusion with potassium nitrate and sodium carbonate) but the frequent cracking of the crucible and consequent expense is a serious drawback. A similar objection applies to Rothe's method (oxidation with nitric acid and magnesium nitrate in glass flasks). A new method is suggested in which the specimen after decomposition with nitric acid and boiling for one hour in the presence of magnesium nitrate is treated with a few drops of bromine, boiled for a further half-hour, and then evaporated nearly to dryness in a dish but not fused. The method, it is claimed, gives satisfactory results, but it is admitted that these are a little low when the rubber contains much combined sulphur. The method has been adopted by the Delft Institute. Many analysts will, however, prefer not to omit heating more strongly, and this presents no difficulties when using magnesium nitrate (the mass does not fuse) if the right make of porcelain dish be chosen. In this connexion reference may be made to the recommendation of A. R. Pearson[58] who completes the oxidation with permanganate.

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[56] Stevens, *Bull. Rubber Growers' Assoc.*, 1919, **1**, 55; *J.*, 1920, **199A.** L. E. Weber, *India-Rubber World*, Nov., 1919, 71; also *India-Rubber J.*, Aug., 1919, *et seq.*

[57] *Netherland Govt. Rubber Inst.*; *cf. J.*, 1920, **665A.**

A. Van Rossem and P. Dekker[59] have made a chemical examination of antimony sulphide as used for rubber compounding. This product is usually sold as containing 15–17% free sulphur which is estimated by extraction with a suitable organic solvent. The authors consider such methods unsuitable, confirming the statement of C. O. Weber that the pentasulphide is thereby decomposed and sulphur liberated. They also reject C. O. Weber's method of dissolving the pentasulphide in ammonia, leaving the free sulphur, on the ground that part of the latter is dissolved. Their method consists in decomposing the antimony sulphide with hydrochloric acid and estimating either the hydrogen sulphide or the free sulphur liberated. Nevertheless the carbon bisulphide extraction figures probably correspond in a rough way with the free sulphur available for vulcanisation, and the figure has been found satisfactory for calculating the amount of additional sulphur, if any, required for vulcanising the rubber. According to Caspari the so-called "crimson sulphide" consists entirely of the trisulphide while the golden sulphide contains 3 to 3·6 atoms of sulphur. Hence at the most it contains about one-third of the pentasulphide. Yet according to Rossem and Dekker's analyses one sample yielded approximately 12% of sulphur from the decomposition of the pentasulphide by extraction with carbon disulphide. Further research is required to clear up these discrepancies and also to prove that the two atoms of sulphur in the pentasulphide which are so readily split off do not behave as free sulphur in vulcanising rubber.

W. K. Lewis and W. H. McAdams[60] have proposed a new method for the direct estimation of the rubber hydrocarbon in raw and vulcanised rubber. Many attempts have been made to do this by converting the hydrocarbon into the tetrabromide and either weighing it or determining the bromine absorbed from a known excess. The reaction involved is not, however, entirely one of addition—some substitution takes place, or HBr is split off from the brominated molecule particularly on prolonged treatment with bromine or, as shown by Schmitz, with rubber which has been degraded by long treatment with a solvent. This must always be the case with vulcanised rubber, where the preparation of a solution without decomposing the rubber necessitates prolonged and careful heating. Any hydrobromic acid liberated in the reaction is therefore determined by adding iodate to the solution and titrating the liberated iodine. The process worked satisfactorily with raw rubber using carbon tetrachloride as solvent. In the case of vulcanised rubber the difficulty of preparing a " solution " was overcome by using tetrachloroethane as solvent. A correction was also necessary to allow for the hydrocarbon saturated with sulphur (sulphur of vulcanisation) and which therefore could not combine with the bromine. The results obtained in several analyses agree quite well with the actual amount of raw rubber present.

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[58] *Analyst*, 1920, **45**, 405; *J.*, 1920, 827A.

[59] *India-Rubber J.*, 1920, **60**, 905; *J.*, 1920, 791A.

[60] *J. Ind. Eng. Chem.*, 1920, **12**, 673; *J.*, 1920, 578A.

To avoid the difficulty of " dissolving " vulcanised rubber and separating the mineral constituents Pearson[61] recommends the use of glacial acetic acid when it is desired to estimate carbonates, oxides, and similar fillers. Ordinarily the surrounding film of rubber protects these substances from attack by mineral acids but acetic acid swells and penetrates the rubber. For the estimation of sulphur on these lines a mixture of acetic and hydrochloric acid is recommended. As is well known, solvents such as ether swell vulcanised rubber and similarly enable acids such as hydrochloric acid to reach the mineral constituents.[62]

S. W. Epstein and R. L. Moore[63] determine cellulose in vulcanised rubber by dissolving other organic constituents by heating with cresol for 4 hours at 160°–185° C. The washed and dried residue containing the cellulose and mineral matter is acetylated and rewashed. The loss on acetylation represents the cellulose. If leather is present 70% is removed, but it is advisable in such a case to digest at a lower temperature and for a longer period.

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[61] *Analyst*, 1920, **45**, 406 ; *J.*, 1920, 827A.

[62] *Analyst*, 1915, **40**, 275.

[63] *India-Rubber J.*, 1920, **59**, 559 ; *J.*, 1920, 343A.

LEATHER AND GLUE.

By F. C. Thompson,

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In last year's Report mention was made of the great interest shown by leather manufacturers in scientific progress and research. It is gratifying to be able to say this year that this interest has not ended with the war but shows every sign of being permanent. Two Leather Trades' Conferences[1] were held during 1920 at which both manufacturers and chemists were represented. Papers were read on numerous subjects, including "Unsolved Problems in the Leather Industry," "Recent Research in Leather Manufacture," "Practical Difficulties in Chrome Tanning," "The Educational Outlook," etc. Discussions followed, and there can be no doubt that such meetings as these help to create excellent working relations between manufacturers and their chemists. Two other events of great importance must be mentioned. The British Leather Manufacturers' Research Association is now definitely established, and Dr. R. H. Pickard, F.R.S., has been appointed Director of Research; work is now in progress. The other event is the opening of a department of leather technology as part of the Northampton Technical School.[2] This department is under the direction of Mr. D. Woodroffe, M.Sc., and will deal with both the scientific and practical aspects of tanning. The crowded state of the previously existing schools at Leeds and London has made the opening of this third school very desirable, quite apart from the special needs of the Northampton district. These events are all evidence of development, and when, in addition, we find individual tanneries providing technical classes for their employees,[3] we may confidently look forward to progress in leather manufacture comparable with that already made in other industries.

Unfortunately, 1920 has been a bad year commercially. The volume of trade began to diminish quite early in the year, and for many months short time has been the rule in tanneries. The causes of this depression are no doubt similar to those affecting other industries, and cannot be discussed in a technical report. It would be pleasant to point to signs of recovery, but at the moment these are few and indefinite. Such a state of affairs has naturally had a serious effect on industrial enterprise. In many cases the adoption of new lines of manufacture has compensated somewhat the failure of the old. As a rule, however, development has been rendered almost impossible. It is to be hoped that the period of depression may pass without causing serious distress. The decontrol of hides took effect on February 29, but subsequent prices of raw materials, leather, and leather goods were much more affected by the commercial situation than by this event. Compared with those prevailing at the beginning of 1920 prices are now very much lower. Indeed in many cases it is most difficult to sell leather or leather goods at all without incurring serious loss. Trade difficulties are not confined to this country. In India, where there have been expectations of a great and developing industry, some works have been compelled to close down, and others have greatly reduced their output. There appears to be little likelihood that the old Indian kip trade will come back to England. It is not certain that tanners are anxious to have it, and further, works erected in Bengal alone from 1917 to 1919 can deal with 2,000,000 hides annually.[4] It is stated that this trade will stay in India or go back to Germany.

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[1] *Leather Trades' Rev.*, 1920, **53**, 66, 1055.

[2] *Ibid.*, 736.

[3] *Ibid.*, 300.

The Weights and Measures (Leather Measurement) Act of 1919 is now in force, and it is a criminal offence to sell a 12-foot skin as containing 12½ feet.[5] The new regulations of the Swedish Government must be mentioned since these prohibit the weighting of imported sole leather by any unnecessary materials such as dextrin, glucose, mineral salts, excess tannin, etc. The ash of imported leather must not exceed 3½%, nor the water-soluble matter 20% in the case of bends or 25% in bellies. No one can question the right of a Government to combat the adulteration of any product, but the difficulty in this case is as to how the water-soluble matter is to be determined. Everything depends upon the exact procedure, and there is no guarantee that the Swedish Government's chemists will decide to adopt the methods used in England. The whole question is being taken up by the Society of Leather Trades' Chemists and the Tanners' Federation with good hopes of an amicable settlement. Finally, it may be mentioned that in spite of the progress made in making the leather industries more savoury, the Penzance Town Council has succeeded in obtaining an order including tanning and leather dressing amongst offensive trades.[6] A tannery conducted on modern principles should offend no one, and it is a matter for regret that some backward establishments should cause an evil reputation to linger.

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[4] *Leather Trades' Rev.*, 258, 872.

[5] *Ibid.*, 18.

[6] *Ibid.*, 212.

UNHAIRING, DELIMING, AND BATING.

Liming and Unhairing.—Not a great deal has appeared on this subject during 1920. H. G. Bennett[7] further develops his views on the lyotrope influence of dissolved salts and other substances on the swelling of hide and gelatin and extends these views to an explanation of the various wet work processes, including liming. Interest is being shown in enzyme unhairing on the practical scale as is indicated by a lecture by C. S. Hollander[8] to the Annual Meeting of the American Leather Chemists' Association on Röhm's now well known "Arazym" method. Hollander claims that the process is notably rapid and clean, and that there is no difficulty in disposing of the waste liquors. An excellent leather results, and the hair removed has an enhanced value as a by-product, being of a glossy texture and absolutely unharmed in structure. The present writer has found tryptic unhairing very easy on the small scale, and an interesting point is that it is often possible to remove hair and epidermis together in a sheet, no doubt in consequence of partial digestion of the *rete mucosum.* At least one patent process for keeping lime liquors in constant circulation has been described during 1920,[9] and the "Forsare" process referred to in the last Report[10] is now advertised and probably coming into wider use. P. Riemer[11] describes a liming process in which skins are first treated with a weak lime liquor containing a little sulphide and then with stronger liquors of pure lime. A. Rogers[12] patents a method for removing the dermal armouring and epithelium of shark skins by the use first of hot fluids, and then of a mixture of lime and sodium sulphide.

Deliming.—G. Grasser[13] has investigated the speed of deliming by various acids etc. Comparative tests with ½% solutions gave the following order of efficiency : sulphuric acid, sulphuric acid and common salt, sulphuric acid and bisulphite, hydrochloric acid, ammonium chloride, hydrochloric acid and common salt, sodium bisulphate, lactic acid, acetic acid, sodium bisulphite, Neradol ND, molasses, and distilled water. It is surprising that sulphuric acid should be more rapid in action than hydrochloric acid, which has the lower molecular weight and greater diffusing and ionising properties, and which gives a much more soluble calcium salt. There is no obvious explanation. Other experiments by Grasser show that the speed of deliming is very little influenced by the mode of the previous liming. Amongst patented processes for deliming are the use of neutral or acid sulphite-cellulose waste lyes[14]; the use of sulphur dioxide at 30°–35° C.[15]; and the use of waste liquors obtained from lupins after removal of the bitter principle.[16] It is very doubtful whether anything is gained by patenting processes such as these, which may work perfectly well under proper conditions, but which involve no new principle. Any substance which reacts with lime to give soluble compounds and has no excessive swelling or other harmful effect on hide can be used for deliming, and there is little gain in abandoning weak acids or ammonium salts for other substances often less convenient in use and more difficult to obtain.

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[7] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 75 ; *J.*, 1920, 418A.

[8] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 477.

[9] E.P. 151,387 ; *J.*, 1920, 758A.

[10] *Ann. Repts.*, 1919, **4**, 349 ; E.P. 124,992 ; *J.*, 1919, 431A.

[11] U.S.P. 1,331,723 ; *J.*, 1920, 308A.

[12] U.S.P. 1,338,331 ; *J.*, 1920, 497A.

[13] *Chem. Zentr.*, 1920, **91**, II., 351 ; *J.*, 1920, 418A.

Bating.—In a former report[17] the view that bating consists largely in the removal of elastin was mentioned. This has recently been much discussed and has been strongly supported by A. Seymour-Jones[18] and J. A. Wilson.[19] The latter has published photomicrographs of skin sections made at various stages of the bating process. The elastic fibres, which lie near the grain of the pelt, are stained with magenta, and certainly diminish in number very largely as bating proceeds. The present writer has seen the actual photographs, which show this effect with exceptional clearness. Wilson states finally that the bating process has two essential features: (1) the reducing of limed skins to the fallen, flaccid condition, and (2) solution or digestion of elastic fibres. There appears to be no doubt that elastic fibres are digested by tryptic enzymes under the conditions of bating. Experiments confirming this have been carried out at Leeds University by R. H. Marriott, who has used both magenta and Weigert's stain in various trials. One difficulty in accepting this behaviour as an essential part of bating is that the digestion appears to require a longer time than is used in practice. In Wilson's experiments, elastin had not disappeared from calf-skin in 20 hours of treatment with trypsin. After 6 hours only part of the fibres had gone. It will be necessary to examine sections from skins puered or bated in the ordinary course of leather manufacture before this question can be settled. The present writer has seen elastin still present in skin decidedly over-bated with an enzyme preparation. A very interesting experiment was carried out by Seymour-Jones and J. T. Wood, in which use was made of the fact that elastin is present only near the grain of skins, and not at all in the bulk of the corium. A sheepskin was split to give a thin grain and a thicker flesh portion. Each piece was divided into two. It was found that enzyme bating and simple acid deliming had the same effect on the flesh split, which contains no elastin. The grain split, however, showed a great difference, the bated portion yielding a soft even-grained leather, whilst the simply delimed piece gave leather with harsh contracted surface. Seymour-Jones concludes therefore that bating is necessary only for the grain side of a skin. This experiment certainly lends support to the theory described above. An objection to the theory that has been raised is that the elastin of *ligamentum nuchae* is resistant to trypsin. If this is an indisputable fact (which is hardly the case according to some experiments carried out at Leeds) it does not necessarily mean anything, since it must first be established that this elastin and that of the elastic fibres are chemically identical, and also what the behaviour of fully limed *ligamentum nuchae* may be. The previous treatment of proteins with acids, alkalis, pepsin, etc. has great influence on the possibility or otherwise of tryptic hydrolysis, as is shown by the behaviour of collagen.

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[14] G.P. 320,301; *J.*, 1920, 578A.

[15] E.P. 125,362; *J.*, 1920, 165A.

[16] G.P. 317,804; *J.*, 1920, 460A.

[17] *Ann. Repts.*, 1918, **3**, 325.

[18] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 60.

[19] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 605.

Mention may here be made of a process patented by F. Rampichini,[20] in which enzyme bates are prepared from glands etc. containing lipolytic and proteolytic enzymes. The materials are treated with common salt, triturated, dried at 40° C., and preserved with small amounts of antiseptics, *e.g.*, salicylic acid. The bate is to be used in conjunction with a deliming material.

TANNING, TANNING MATERIALS, ETC.

Numerous processes have been patented but none appears to be especially noteworthy. As they cover the whole range of tanning an account of them cannot but be somewhat disconnected.

Vegetable Tanning.—A. Ringbauer [21] has patented a process for vacuum tanning in which hides are stretched on frames in closed vessels which are then exhausted. Tan liquor is introduced without admitting air, and tanning then proceeds. H. R. Procter[22] refers to the Nance process for vacuum tanning and points out that in its latest modification emphasis is laid on an essential point sometimes rather overlooked, *i.e.*, that wet hides must be in such a vacuum that the liquid actually boils, and the pores of the leather are filled only with vapour at very low pressure. Then, when tan liquor is introduced and air subsequently admitted, the great increase in pressure causes the liquor to be sucked into the hide.

Patents by H. B. Landmark[23] and by W. Mensing[24] describe the preparation of tanning liquors from sulphite-cellulose waste liquors.

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[20] E.P. 124,718; *J.*, 1920, 633A.

[21] G.P. 321,343; *J.*, 1920, 666A.

[22] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 28.

[23] U.S.P. 1,327,105; *J.*, 1920, 200A.

[24] G.P. 304,349; *J.*, 1920, 274A.

According to the latter inventor, the lye is heated with oxidising agents, *e.g.*, chlorates, nitrates, permanganates, etc.

A process which scarcely represents an advance, but rather a retrogression in leather manufacture, consists in tanning hides with cutch and zinc sulphate, the latter in large proportion.[25] Leather of this kind would usually be regarded as adulterated.

Syntans.—Several new substances of this class are described in patents, but almost all are the now familiar condensation products of aromatic substances and formaldehyde, the conditions of the condensation being such that only soluble products are formed.[26] An excellent account of syntans is given by G. Grasser in his recent book, "Synthetische Gerbstoffe," a work which is not a mere compilation, but which is written with a great deal of special knowledge of the subject. Grasser describes many syntans which are products of condensations carried out without formaldehyde, but no new patent describing products of this type has come to the writer's notice during 1920. The Deutsch-Koloniale Gerb- und Farbstoff-Ges. describe a process of tanning by producing a syntan in the pelt.[27] Hides are immersed alternately in baths of 2–5% formaldehyde and of aromatic compounds capable of giving an insoluble compound with formaldehyde. Such substances are α-naphthylamine and resorcinol. In this way substances possessing tanning properties but too insoluble to use in solution may be formed in the pelt and thus utilised.

Mineral Tannages.—Iron tanning has again been the subject of patents. K. W. Mensing[28] prepares a tanning solution by the action of oxidising agents on solutions of iron salts. During the preparation of the solution the temperature is not allowed to rise above 35° C. The tanning solution is cooled rapidly and hides are treated at once. Delimed hide may be treated first with faintly alkaline salts, or with basic alum or chrome solutions, and then is tanned in the iron solution, the process being quite rapid. By this means the bad effect of ferrous iron on the leather is avoided, also the subsequent appearance of such iron in the leather, and further, the hydrolysis of ferric salts is prevented. Modifications described in additional patents are claimed to give a better leather in some respects, *e.g.*, give a smoother grain. It is unfortunate that accounts of processes for iron tannage, whether patent specifications or not, rarely say anything about the keeping qualities of the leather produced. It is here that the greatest difficulty lies. Chromium formate liquors of German manufacture were on the market before the war and were reputed to be of great service. W. Clark[29] describes an interesting tanning process using an iron formate liquor: 6 kg. of sodium formate dissolved in 20 litres of water is added to 5 kg. of ferric chloride in the same amount of water; after standing for some time, the liquor is diluted for use. Similar liquors are prepared by slightly modified methods. The tanning of skins is carried out in solutions of sp. gr. 1·02, and is quickly accomplished (4–8 hrs.). The leather, after draining, is cleaned in 1% borax solution, retanned with sulphite-cellulose liquor, and dressed as bark-tanned leather. With regard to chrome tanning it may be mentioned that J. Morel[30] has patented the preparation of a basic chrome liquor of the composition $Cr(OH)SO_4$ by passing sulphur dioxide into bichromate solutions without any addition of acid. This process was referred to in a previous Report[31] as already well known, and sulphur dioxide was included in last year's Report[32] in a list of substances capable of reducing bichromates to give a tanning liquor. It is difficult to see how such a patent as the above can be valid. Papers by E. Griliches and D. Burton, which bear rather on the theory of chrome tanning, will be dealt with later in this Report.

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[25] U.S.P. 1,323,956; *J.*, 1920, 124A.

[26] G.P. 320,613; *J.*, 1920, 666A; 319,713; *J.*, 1920, 553A; 315,871; *J.*, 1920, 378A. E.P. 138,796; *J.*, 1920, 308A. U.S.P. 1,344,950, 1,344,951, 1,344,952; *J.*, 1920, 606A.

[27] G.P. 305,516; *J.*, 1920, 274A.

[28] G.P. 314,487; *J.*, 1920, 124A; 314,885; *J.*, 1920, 199A. Also M. E. and R. Stecher, G.P. 319,705 and 319,859; *J.*, 1920, 553A.

Finishing, Waterproofing, etc.

A few processes for waterproofing leather, etc. have been described but none present any features of special interest. J. J. Byers[33] impregnates dry leather with a cement of soluble nitrocelluloses and non-drying oils. H. Hoffmeister and J. Paessler[34] steep dried lining leathers (from which excess tannin has been washed out) in a solution of wood-tar in benzene or methyl alcohol, in the presence of organic acids. Tawed leather should have a preliminary vegetable tannage before impregnation. This treatment is claimed to increase the wearing properties of the leather. W. Rechberg[35] treats vegetable-tanned leather with solutions of pyridine bases and impregnating materials insoluble in water, *e.g.*, resin, asphalt, rubber in benzene, etc.

A number of mixtures have, as usual, been patented as leather substitutes. Many of these are of the common type, *i.e.*, consist of leather powder, rubber, oils, glue, sulphur, etc., heated together and pressed or shaped.[36] One patent[37] describes the treatment of mill-board with 30% solutions of hygroscopic salts (*e.g.*, zinc chloride); the material is then dried and treated with warm fatty oils and rosin oil. A more interesting process[38] yields a leather substitute of fibrous structure. The bast bark of birch is saturated with waterproofing solutions, *e.g.*, viscose, chromed glue, etc. It is claimed that the original flexibility of the bark is retained.

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[29] E.P. 136,193; *J.*, 1920, 165A.

[30] E.P. 148,615; *J.*, 1920, 626A.

[31] *Ann. Repts.*, 1918, **3**, 329.

[32] *Ann. Repts.*, 1919, **4**, 353.

[33] U.S.P. 1,327,197; *J.*, 1920, 242A.

[34] G.P. 324,495; *J.*, 1920, 793A.

[35] G.P. 317,148; *J.*, 1920, 419A.

In concluding this section of the Report it may be said that nothing amongst actual tanning processes so interesting as the use of colloidal tannin carriers, described in the last Report, has emerged during 1920. In leather finishing the chief feature is, perhaps, the increasing use of pigment finishes, *i.e.*, mineral pigments suspended in a suitable medium which is capable of drying to a hard, bright, resistant film. Such finishes are useful in covering up surface defects in leather, but as chemical principles are not involved in their use they cannot appropriately be discussed here.

ANALYSIS.

Tannin Analysis.—Few analytical papers dealing with tannins have excited so much interest and discussion as that by J. A. Wilson and E. J. Kern[39] on the "true tanning value" of vegetable tanning materials. The authors adopt a new definition of tannin, which is described as that portion of the water-soluble content of a tanning material which will combine with hide fibre and resist washing out with cold water. Their procedure is in accordance with this definition. 12 g. of hide powder of known nitrogen content is shaken for 6 hours with 200 c.c. of tannin solution. If the solution still contains tannin (as shown by the gelatin-salt reaction) the detannisation must be repeated, using less tannin solution. The tanned hide-powder is repeatedly washed with water and squeezed until all non-tannins have been removed as indicated by a negative iron test. Each washing lasts 30 mins., and about 12 washings are necessary. The washed powder is dried for 24 hours at room temperature and then analysed for moisture, fat, and hide-substance (by nitrogen); the amount of combined tannin is the difference between the sum of these three and the weight of tanned powder. Compared with the official methods in use in Europe and America, the new procedure gives very low results, particularly so in the case of non-astringent materials of high non-tannin content, such as gambier. The divergence is far less, though considerable, with an astringent material containing little non-tannin, such as quebracho.

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[36] W. Drury, E.P. 135,921; *J.*, 1920, 166A. G. Christenson, U.S.P. 1,332,320; *J.*, 1920, 343A. H. Blücher and E. Krause, G.P. 314,728; *J.*, 1920, 242A.

[37] D. Waller, G.P. 315,434; *J.*, 1920, 343A.

[38] v. Heynitz, G.P. 320,629; *J.*, 1920, 633A.

[39] *J. Ind. Eng. Chem.*, 1920, **12**, 465; *J.*, 1920, 522A.

Material	% tannin by American official method.	% tannin by Wilson's method.
Quebracho	68·0	47·4
Hemlock bark	10·1	6·2
Chestnut wood	25·8	11·9
Sumach	25·6	9·6
Gambier	25·0	7·8

The method is obviously long and troublesome, but the authors claim that the results it gives are true and that excellent duplicates can be obtained. These advantages, it is claimed, should outweigh other considerations. Naturally, this method has been subjected to much criticism. It is urged that the ageing of tannins on the fibre is ignored, and that much of what is washed out is capable of tanning. The most serious criticism yet brought forward is that of G. W. Schultz and T. Blackadder,[40] and to their paper readers interested must be referred. All that can be said here is (1) that the finer particles of powder are more heavily tanned than the bulk, and are partly lost in the washing; (2) that by concentrating the washings a tanning solution can be obtained; (3) that on account of the way in which tannin is determined there is always a probable error of eight times the error in nitrogen estimation; (4) that there is always a discrepancy between the total solids of the original tannin solution and the tannin found, plus the total solids of the washings. Wilson considers with regard to objection (2) that non-tannins in part are converted into tannins by boiling with water, and supports this very reasonable view by experiments. Wilson's statement that the present official methods cannot account for the tannin used in a yard was contested in a discussion by several chemists, who claimed that 92–94% could be accounted for. This, for fermentable materials used in so long a process, must be regarded as sufficiently close control.

The modified method of tannin analysis proposed by G. Baldracco was referred to in the last Report.[41] Baldracco has replied[42] to J. G. Parker's criticisms,[43] and claims that whereas non-tannin filtrates obtained by the official method often contain tannin, the filtrates obtained by his modified method are always free from tannin as tested by his gelatin-acetic acid reagent which he claims to be more delicate than the ordinary gelatin-salt reagent. E. Schell,[44] however, criticises the modified method on the grounds that too much hide powder is used and that there is greater absorption of non-tannins than by the official method.

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[40] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 654.

[41] *Ann. Repts.*, 1919, **4**, 355 ; *J.*, 1920, 123A.

[42] *J. Soc. Leather Trades Chem.*, 1920, **4**, 110 ; *J.*, 1920, 523A.

[43] *Ibid.*, 1919, **3**, 199 ; *J.*, 1920, 123A ; *Ann. Repts.*, 1919, **4**, 356.

Several useful papers on qualitative tannin analysis have appeared recently. E. Schell[45] reviews the tests for mangrove in mixed extracts and points out that none of them, including his own test, is absolutely reliable under any circumstances that may obtain. R. Lauffmann[46] describes a simplified method for determining the molybdenum figure for tannins : 10 c.c. of clear tannin solution of four times analytical strength is mixed with 10 c.c. of the special reagent and filtered. The total solids in the filtrate are determined by evaporation and subtracted from the solids similarly determined of an equivalent amount of tannin solution plus reagent. The percentage precipitated by the molybdenum reagent is thus readily found. This figure may vary from 2, sometimes, with quebracho extract, to 194 with chestnut wood extract. Lauffmann[47] has a further paper on the detection of artificial tannins and gives an improved form of the indophenol test of Seel and Sander.[48] A. Harvey[49] has investigated the sugar content of Natal mimosa barks and pure extracts. In the latter 2·2–4·4% of monosaccharides and 3·2–7·2% of disaccharides were found, a somewhat surprising amount. The Customs authorities levied duty when extracts contained over 4% of disaccharides.

W. R. Atkin and F. C. Thompson[50] describe a rapid indicator method of determining the true acidity or hydrion concentration of tan liquors. Use is made of the well-known comparator of Walpole, in which the colours given with indicators in unknown solutions are matched with those obtained with standard buffer solutions of definite acidities. Except with very dark liquors the matching is quickly accomplished. The acidity thus found is a direct indication of swelling power, and is helpful in some cases when lime-water titration figures are useless. The method is, of course, not so accurate as the electrometric determination of hydrogen ions, but requires only ordinary apparatus and can be easily understood.

Leather Analysis.

The sub-committee appointed by the British Section of the Society of Leather Trades' Chemists has investigated very thoroughly the extraction of grease from dressing leathers by various solvents.[51] The conclusion arrived at is that benzene and chloroform give the most complete extraction, and that the latter should be adopted since it is already prescribed for use by the members of the American Association. The only disadvantages are cost and the fact that a rather dark extract (probably containing a little tannin) is obtained. Petroleum ether can no longer be used as it invariably gives low results.

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[44] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 220 ; *J.*, 1920, 666A.

[45] *Ibid.*, 1918, **2**, 284 ; *J*, 1920, 496A.

[46] *Ledertechn. Rundsch.*, 1919, **11**, 93 ; *J.*, 1920, 343A.

[47] *Collegium*, 1920, 169 ; *J.*, 1920, 729A.

[48] *J.*, 1916, 1028.

[49] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 11 ; *J.*, 1920, 242A.

[50] *Ibid.*, 1920, **4**, 143 ; *J.*, 1920, 605A.

Another sub-committee has worked on chrome leather analysis.[52] The results are largely numerical and cannot be summarised here, but attention may be drawn to two interesting points: (1) the basicity (Cr : SO_4=52 ; x) of the chrome compound on the leather fibre is about 70–80 in the case of two-bath leathers, but only about 40 in the case of one-bath leathers, and (2) soap used in fat-liquoring reacts to form an acid chrome soap insoluble in water, but soluble in petroleum ether. These are important results of considerable theoretical importance. The determination of the basicity mentioned above was made by estimating chromium and sulphuric acid in the fat-free, water-extracted leather.

One or two papers deal with the determination of nitrogen in leather by Kjeldahl's method. J. Kahn[53] and P. Chambard[54] agree that one of the great difficulties lies in obtaining a fair sample of the leather. The latter not only recommends that the sample should be very finely ground, but that the large amount of 2·8 g. should be weighed out for digestion. This is about four times the usual quantity used. In the opinion of the present writer the only difficulty peculiar to leather analysis in Kjeldahl determinations is in the sampling. Questions of oxidising agents etc. matter very much less. F. Enna[55] recommends mercury as a catalyst to hasten the digestion. In the writer's experience the process is quite reasonably rapid if the sulphuric acid is kept briskly boiling. Loss of acid is only small if a funnel is inserted in the neck of the flask.

An interesting method, due to A. W. Thomas,[55a] for the determination of free sulphuric acid in leather, depends on the power of ions of higher valency to displace those of lower valency from their adsorption compounds. Leather containing sulphuric acid is heated with a solution of acid potassium phosphate, and sulphates are then determined in the extract. Correction is made for neutral sulphate present in the original leather.

[51] *Ibid.*, 1920, **4**, 7, 300.
[52] *Ibid.*, 1920, **4**, 294.
[53] *Collegium*, 1920, 367 ; *J.*, 1920, 731A.
[54] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 159 ; *J.*, 1920, 605A.
[55] *Collegium*, 1920, 207 ; *J.*, 1920, 730A.
[55a] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 504.

Miscellaneous Analysis.

A sub-committee has been appointed to deal with limeyard control. So far the work has been largely of an investigational character, and no attempt has yet been made to fix standard methods. F. C. Thompson and W. R. Atkin[56] found that the precipitates obtained (1) when a used lime liquor was neutralised with hydrochloric acid, and (2) when a liquor was neutralised with acetic acid and half-saturated with common salt, were both due to hydrolysed keratinous matter and did not arise from true hide substance. This was shown by control experiments with gelatin, hide-powder, and hair. In the case of pure keratin, roughly one-half was precipitable. D. Burton[57] contributed a comprehensive review of previous work on the subject of limeyard control, with a full list of references. Depilation, swelling, solvent action on the epidermis and interfibrillary substance, and removal of fat are the general objects of liming. Solution of true hide substance is rarely desired. Burton points out that depilatory power can only be estimated by determining sulphides present and considering the bacterial condition of the liquor. Swelling power depends on true caustic alkalinity, and not on total alkalinity involving bases combined with weak acids. Solvent action on hide substance depends on the gelatin-liquefying bacteria present. W. R. Atkin and W. E. Palmer[58] corrected Bennett's formaldehyde method for the important determination of caustic alkalinity. The amended method is in outline as follows: (1) Neutral formaldehyde is added to clear lime liquor, and the mixture then titrated with acid; the acid neutralises calcium and sodium hydroxides, and sodium hydroxide produced by interaction of formaldehyde and sodium hydrosulphide; ammonia gives a neutral compound with formaldehyde, and amino-acids produce strong acids which partly neutralise the lime liquor before titration commences. The titration measures, therefore, original caustic alkalinity, plus hydrosulphides, less amino-acids. (2) Filtered lime liquor is neutralised to phenolphthalein, sulphides are removed by iodine. Formaldehyde is again added and the solution is titrated with alkali. This time the formaldehyde reacts with ammonium chloride to give hydrochloric acid, and the amino-acids again yield strong acids. This titration thus gives ammonia plus amino-acids. If the two titrations are added together we have a measure of caustic alkalinity, sulphides, and ammonia, since the amino-acids cancel. Ammonia and sulphides can be separately determined and thus the caustic alkalinity is found. This is an interesting example of the difficulties met with in analysing partially hydrolysed protein solutions. W. R. and J. Atkin[59] have described another method for the determination of caustic alkalinity. A solution of sodium hydrosulphide about $N/20$ in strength hydrolyses to such an extent that the alkalinity corresponds to $p_H = 10{\cdot}0$. This corresponds to $N/10{,}000$ in strong alkali, and ammonia is (roughly irrespective of dilution) neutralised to the extent of 24% at this point. The lime-liquor is therefore titrated with hydrochloric acid until the alkalinity $p_H = 10$ is reached. Thymolphthalein is used as indicator, and the colour matched in the comparator with that given by a standard solution of the desired reaction. A suitable solution is a mixture of 76% $N/10$ ammonia and 24% $N/10$ ammonium chloride. In titrating, all of the caustic alkali is neutralised, except sufficient to make the solution $N/10{,}000$ in strength (0·1 c.c. $N/10$ NaOH per 100 c.c.), the hydrosulphide is unaffected, and 24% of the free ammonia is neutralised. As stated above, the free ammonia can be independently determined, so that a new method is provided for caustic alkalinity. The two methods agree excellently :—

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[56] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 15; *J.*, 1920, 242A.

[57] *Ibid.*, 1920, **4**, 32; *J.*, 1920, 307A.

[58] *Ibid.*, 1920, **4**, 111; *J.*, 1920, 145T.

Lime liquor	1	2	3	5
Method I.	10·1	13·2	15·7	15·55
Method II.	10·2	13·5	15·7	15·35

Results are expressed in c.c. of $N/10$ acid required for 25 c.c. of lime liquor. As part of the work of the same committee, J. E. Pickles[60] has introduced another method for determining sulphides in lime liquors. The liquor is decomposed with acid, and the hydrogen sulphide thus liberated is distilled into cadmium acetate solution. The precipitate of cadmium sulphide is filtered off and decomposed with standard iodine solution, the excess of which is easily determined. The method is rapid, gives excellent duplicates, and does not include sulphur dioxide from thiosulphates in the sulphide determination as do some other processes, *e.g.*, Mohr's.

The determination of the basicity of chrome liquor (*i.e.*, SO_4 combined with chromium and therefore hydrolysable) has been discussed by B. B. Dhavale and S. R. Das[61] and by D. Burton and A. M. Hey.[62] The former authors find that the titration figure with alkali, and consequently the amount of SO_4, is increased if sodium chloride is added to the liquor until 300 parts of salt are present to one part of chromium. Further addition of salt has no effect. This is a result difficult to understand. It is now well known that sodium chloride gives a marked increase in hydrogen ion concentration of a chrome liquor, but this does not explain an increase in titratable acid. The increase obtained, however, was quite considerable and amply confirmed. Burton and Hey suggest that the

[59] *Ibid.*, 1920, **4**, 236 ; *J.*, 1920, 758A.

[60] *Ibid.*, 1920, **4**, 231 ; *J.*, 1920, 758A.

[61] *Ibid.*, 1920, **4**, 225 ; *J.*, 1920, 758A.

[62] *Ibid.*, 1920, **4**, 272.

titration with alkali be commenced in the cold and only finished at boiling temperatures in order to include volatile acids such as carbonic and sulphurous acids, which certainly function in tanning with a liquor containing them. The modified method gives the same results as the old one when no volatile acids are present.

G. Grasser[63] determines lime in pelt by dissolving the material in hot dilute nitric acid and estimating calcium as oxalate.

THEORY OF TANNING, ETC.

Chemistry of Tannins.—K. Freudenberg is continuing the work begun with Emil Fischer on the chemistry of tannins, and has published several papers, each marking a distinct advance. Chlorogenic acid, the tannin-like constituent of coffee, is shown[64] to be a simple depside of caffeic and quinic acids, the carboxyl group of the former being united to one of the hydroxyl groups of the latter:

$$C_6H_3(OH)_2.CH:CH.CO.O.\ C_6H_7(OH)_3\ COOH.$$

This comparatively simple structure partly explains how "coffee-tannin" resembles the tannins. It gives many of the reactions but does not tan pelt. Chlorogenic acid is resolved by tannase and by some moulds into its constituent acids. Hamameli tannin[65] is proved to be an ester-like compound of two molecules of gallic acid and one of an aldo-hexose so far not identified. This conclusion was arrived at previously,[66] but is now confirmed. Gambier catechin[67] is shown to have an oxydiphenylpropane skeleton and not to be a derivative of ethyldiphenylmethane as Kostanecki supposed. This brings catechin into line with the nearly related flavone dyes and anthocyanidins. Chebulinic acid[68] from myrobalans gives a crystalline substance by the action of hot water, which is definitely proved to be a digalloylglucose. The amorphous acid produced simultaneously appears to have the formula $C_{14}H_{14}O_{11}$, and gives pyrogallol when heated under reduced pressure.

G. Grasser[69] has carried out a long series of experiments on the electrical nature of tannins in solution. All tannins, with the exception of quebracho, migrate to the anode in acid solution, and are therefore negatively charged. In many cases the migration was sluggish or indefinite in the simple tannin solution, and acetic acid was required to bring about normal cataphoresis. Grasser obtained many other interesting results, *e.g.*, he found that mangrove and catechu were sodium salts, and that in some cases a separation of two qualitatively different tannins could be effected by electro-osmosis. The subject is rendered very difficult by decompositions and secondary changes, and also, of course, by the complexity of the original substances. Tannins have only been adequately purified in two or three instances, and more work on these lines seems to be necessary before electrical properties can be very profitably studied. Grasser concludes from his experiments that the passage of an electric current through tan liquors should facilitate tannage.

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[63] *Collegium*, 1920, 80; *J.*, 1920, 730A.

[64] *Ber.*, 1920, **53**, 232; *J.*, 1920, 274A.

[65] *Ibid.*, 1920, **53**, 953; *J.*, 1920, 523A.

[66] *Ann. Repts.*, 1919, **4**, 360; *Ber.*, 1919, **52**, 177; *J.*, 1919, 296A.

[67] *Ber.*, 1920, **53**, 1416; *J.*, 1920, 729A.

[68] *Ber.*, 1920, **53**, 1728; *J.*, 1920, 792A.

[69] *Collegium*, 1920, 17, 49, 137, 200, 277, 332; *J.*, 1920, 729A.

Grasser has also written a paper on synthetic tannins[70] in which he points out what is often overlooked, namely that the power of precipitating gelatin is not always accompanied by tanning properties. An example is hydroxynaphthylmethanesulphonic acid. This substance precipitates gelatin but does not tan pelt. Sodium dicresylmethanedisulphonate will neither precipitate gelatin nor tan pelt, but is readily absorbed by hide powder. Again, *o*-nitrophenol tans pelt and is absorbed by hide powder, but will not precipitate gelatin. It is indeed very difficult, if not impossible, to fix a rigid and yet adequate definition for tannins. It is scarcely reasonable to expect investigators in chemistry etc. to carry out pelt tests, but it is obviously unwise to infer too much from the behaviour with gelatin solutions. The main part of Grasser's paper consists of descriptive matter given more fully in his book on the same subject.

Chemistry of Hide and Gelatin.—Moeller[71] takes the view that the action of acids on hide powder is first one of hydrolysis, which is much more marked and rapid with inorganic than with organic acids. This view appears to the writer to be totally unjustifiable. The whole trend of work done in recent years on the physical chemistry of proteins has been to show that proteins, like amino-acids, are amphoteric compounds capable of combining with either acids or alkalis according to circumstances. Gelatin for instance has its iso-electric point at $p_H = 4{\cdot}6$. In solutions more acid than this the gelatin combines with acids to form salts such as the hydrochloride; in more alkaline solutions it combines with bases to form gelatinates. Loeb's work alone amply proves this. Hydrolysis only begins with raised temperatures or stronger solutions of acids and alkalis, but of course every protein differs in susceptibility from the rest. There can be very little if any hydrolysis in the case of hide powder and $N/10$ acids at ordinary temperatures. In any case, hydrolysis is not the first action, as Moeller claims. Moeller goes on to say that the presence of neutral salts at first checks this hydrolysis and then suddenly facilitates it. Considerations of this kind are used to contest the chemical theory of tanning. Moeller is, no doubt, on right lines when he emphasises the differences between gelatin and hide-powder. Both are certainly proteins and have the general characters of their class, but it has been too readily assumed in the past that the difference between the two was only a water molecule.

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[70] *Ibid.*, 1920, 234 ; *J.*, 1920, 729A.

[71] *Ibid.*, 1920, 109, 152, 209, 267, 319, 382 ; *J.*, 1920, 730A.

Important work on the swelling of gelatin has been done by Miss D. J. Lloyd,[72] whose paper is of considerable length and brings out several interesting points. Miss Lloyd concurs in the view above stated that at $p_H < 4·6$ gelatin acts as a base to form soluble, ionisable salts, *e.g.*, hydrochlorides, and at $p_H > 4·6$ as an acid giving gelatinates with soda etc. An important point is that Miss Lloyd finds sodium gelatinate to be irreversible, *i.e.*, gelatin in its original form cannot be recovered from it, although careful experiment failed to show any signs of hydrolysis. This may prove to have bearing on the liming of hides and skins. The explanation suggested in harmony with H. D. Dakin's view of protein racemisation is that there is an internal structural change of the keto-enol type at the peptide linkages : $-CO{\cdot}NH- \rightarrow -C(OH):N-$.

Under the action of acids gelatin goes to the keto form; alkalis favour the enol form. With regard to the structure of gelatin jellies, Miss Lloyd speaks of a solid framework of neutral gelatin with interstices filled with a solution of gelatin in the salt form. This is the two-phase theory which H. R. Procter opposes,[73] holding that an open network of microscopic dimensions would allow perfectly free diffusion without any development of osmotic pressure or cause for swelling. Procter's own view is that jellies have a solid, possibly crystalline, framework of molecular dimensions, from which ions cannot diffuse since they are always within the range of electrochemical attractions. F. G. Donnan's membrane-potential theory also requires such a structure. Miss Lloyd has examined the swelling of gelatin in solutions varying from $p_H = 1$ to $p_H = 13$ and finds (1) a maximum at $p_H =$ about 2·4 in acid solutions, (2) a minimum at $p_H = 4·6$, the isoelectric point, (3) a region of slow increase of swelling from $p_H = 4·6$ to $p_H = 10$, which includes the point of absolute neutrality, $p_H = 7$, and (4) a maximum in alkaline solutions at $p_H =$ about 11·8. This last point corresponds to strong alkali at something less than $N/100$ concentration. There was difficulty in determining the curve for stronger solutions of alkali since hydrolysis intervenes much more than with corresponding solutions of acids.

W. R. Atkin[74] has recalculated the results of several workers on gelatin swelling, and finds that gelatin swelling in acid solutions is always at a maximum at $p_H = 2·4$. This has been shown to be the case even when hydrion concentrations were not determined by the worker himself, but could be calculated from his experimental data. A maximum swelling cannot always be reached with organic acids, *e.g.*, acetic acid. This is because such concentrated solutions are necessary to give the requisite p_H that the gelatin is hydrolysed and dissolved. Procter and Wilson's quantity *e*, which is proportional to the swelling power, is also a maximum at the same hydrion concentration.

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[72] *Biochem. J.*, 1920, **14**, 147; *J.*, 1920, 419A.

[73] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 187.

[74] *Ibid.*, 1920, **4**, 248; *J.*, 1920, 792A.

Chrome Liquors, Chrome Tanning, etc.—D. Burton[75] shows that violet tanning liquors tan more rapidly than green solutions of the same empirical composition, and the explanation is thought to lie in the more acid character of the green liquors due to greater hydrolysis. Violet solutions have often been held to be useless for tanning, though the question has always been somewhat doubtful. Burton also points out a most important fact, namely that the boiling test may be satisfied by chrome leather after neutralisation which would shrink badly if tested before neutralisation. It is, therefore, unnecessary to prolong tannage until the leather taken straight from the liquor will satisfy the boiling test. Indeed, Burton regards this test as too exacting even for neutralised leather. If there is no horniness or curling at the edges of the test piece a small amount of shrinkage may be ignored. Burton finally argues that the tanning properties of a liquor are determined by chromium concentration and acidity, [H·], and not by basicity. E. Griliches[76] has also investigated single-bath chrome tanning. During the first 24 hrs. of tannage the more basic component is absorbed from concentrated violet solutions, and the more acidic component from more dilute solutions. From green as compared with violet solutions the absorbed portion is more acidic. Other results are described, including the finding that violet solutions tan as effectively as green ones.

J. A. Wilson and E. A. Gallun[77] find that many neutral salts, including sodium chloride and sulphate, magnesium chloride and sulphate, and ammonium chloride, all retard chrome tanning in concentrations up to three times molar. Beyond this point the investigation was not carried. In all cases the retardation was considerable; for instance, one pound of common salt added to a gallon of chrome liquor reduced the chromium fixed by 100 g. of hide substance in 3 days from 10·1 to 3·2 g. Here the concentration of chromium and the basicity were unaltered. This diminution in the amount of chromium fixed is attributed to the increase in hydrion concentration caused by the common salt (*cf.* Burton above). This, however, does not account for the action of sulphates which depress the hydrion concentration. The action of magnesium chloride is greatest at molar concentration, the retardation being much less at three times molar strength. This suggests that some such change might take place with other salts.

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[75] *Ibid.*, 1920, **4**, 205; *J.*, 1920, 666A.

[76] *Z. Elektrochem.*, 1920, **26**, 342; *J.*, 1920, 633A.

[77] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 273.

Reference should be made to two papers by A. W. Thomas and M. E. Baldwin[78] on the time factor in the absorption of chromic sulphate by hide. Their results are largely numerical and cannot be given here. They find, however, that the absorption does not correspond with the formulæ for mono-, di-, or tri-molecular reactions.

Aldehyde Tannage and Chamoising.—O. Gerngross[79] confirms Stiasny's statement[80] that hide powder has less power of combining with acid after treatment with formaldehyde than before. The loss in acid absorption shows no regularity with different acids. In the presence of considerable amounts of acid, the reaction between hide and formaldehyde is suppressed. This might, in the writer's opinion, be expected from the behaviour of amino-acids with formaldehyde. The formation of methylene amino-acids is only complete under conditions of considerable alkalinity. The reaction is, in fact, reversible. The experiments of Gerngross show, if not the presence of free amino groups, at least the presence of some groups capable of chemical reaction with formaldehyde. Moeller[81] affirms in reply that formaldehyde combines not with hide but with decomposition products. The tanning agent in formaldehyde consists of insoluble polymers formed on the fibre. Moeller[82] claims from experiments that oil tanning is effected by ozonides.

Glue.

A very important paper on glues and gelatins is due to R. H. Bogue.[83] Much well-known ground is re-traversed and a very full bibliography is given. With regard to the effects of salts etc. on viscosity of solutions, setting points, etc., the author is in agreement with other workers, but cites experiments of his own. He finds that if gel strengths are constant, then viscosity varies as the melting point, and if the normal viscosity remains constant, then the gel strength varies as the melting point. There appears to be no relation between the proximate constitution (peptone content etc.) and the gel strength of glues, except in the case of water content. The various grades etc. of glue differ in composition, impurities from keratin, mucin, chondrin, etc. enter the solution by hydrolysis during the boiling. Hide and bone glues differ in composition.

[78] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 147, 287.

[79] *Collegium*, 1920, 2; *J.*, 1920, 730A.

[80] *J.*, 1908, 413, 580.

[81] *Collegium*, 1920, 185; *J.*, 1920, 730A.

[82] *Ibid.*, 1920, 69; *J.*, 1920, 552A.

[83] *Chem. and Met. Eng.*, 1920, **23**, 5, 61, 105, 154, 197; *J.*, 1920, 605A.

Even gelatin is not pure protein, but contains considerable amounts of proteoses, peptones, etc., a fact not often recognised by workers using gelatin. The usual method of purification by soaking in acid and dialysing will, no doubt, effectively remove inorganic bases and salts, but not proteoses, or proteins present as impurity. Gelatins are prepared by boiling with water, the action of which may last for days. Obviously, hydrolysis takes place continuously, and the resulting product, even if derived from a pure protein, must contain proteins in various stages of hydrolysis. Bogue recommends the melting point method for the evaluation of glues as yielding true evidence of strength in use.

Several forms of apparatus for measuring the strength of glue jellies have been described. In one case a torsion dynamometer is used[84] for measuring the strength of cylindrical test pieces. No relation could be established between gelatin content and strength, as thus determined. G. Hopp[85] determines the tensile strength of strips 7 in. by 0·1 in. by 0·33 in. in dimensions prepared by drying a jelly in air under pressure. W. H. Low[86] describes a modification of the Smith glue tester.

F. L. Browne[87] describes the analysis of casein intended for making waterproof glues. The determinations suggested are those of fineness, ash, moisture, fat, nitrogen, and acidity. Moisture is found by drying *in vacuo* at 70°–80° C. For acidity, the casein is dissolved in standard alkali and titrated with acid, using phenolphthalein as indicator. The other determinations are made in the usual way. The requirements of U. S. specifications are given. S. Butterman[88] found the ash content to be the chief variant in samples of casein, and that this necessitated a corresponding variation in the amount of water required to give glues of similar consistency, according to the formula $y = mx + c$, where m and c are constants determinable from a graph.

An ingenious process is patented by H. Grünewald[89] for a water-resistant glue. Animal glue is mixed with the products of interaction of albumin and formaldehyde. Heat and pressure cause the liberation of formaldehyde from part of the mixture and the glue is acted upon and rendered insoluble. A glue substitute[90] is described, prepared by the action of acids on starch and subsequent treatment with formaldehyde. The product is claimed to be as effective as animal glue.

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[84] S. E. Sheppard, *J. Ind. Eng. Chem.*, 1920, **12**, 1007 ; *J.*, 1920, 758A.

[85] *Ibid.*, 1920, **12**, 356 ; *J.*, 1920, 378A.

[86] *Ibid.*, 1920, **12**, 355 ; *J.*, 1920, 378A.

[87] *Ibid.*, 1919, **11**, 1019 ; *J.*, 1920, 124A.

[88] *Ibid.*, 1920, **12**, 141 ; *J.*, 1920, 274A.

[89] G.P. 317,963 ; *J.*, 1920, 497A.

[90] Farbenfabr. vorm. F. Bayer u. Co., G.P. 318,957 ; *J.*, 1920, 578A.

AGRICULTURAL CHEMISTRY.

By E. J. RUSSELL, F.R.S.,

Director of the Rothamsted Experiment Station.

DURING the year 1920 there has been a continuation of the process which for some time past has been at work in this country—the concentration of agricultural research work at a few institutes, with consequent cessation or suspension of the activities of other places. Widespread regret is felt at the closing of the Woburn Fruit Farm which, since 1893, has been the centre of much important work on fruit trees: this step was taken in consequence of the death of Mr. S. U. Pickering after a long and painful illness. At the moment of writing it appears, also, that the Woburn Experimental Farm of the Royal Agricultural Society may be closed. If this were done it would indeed be most regrettable, but vigorous efforts are likely to be made to keep it open. On the other hand, the expansion of Rothamsted and Cambridge still continues, and further progress has been made with the investigations of soils, plant nutrition, plant pathology, and animal nutrition.

In the present report it is proposed, as before, to confine attention to the technical aspects of the subject, the more scientific aspects being dealt with in the Report of the Chemical Society.

FERTILISERS.

Probably at the present time the most important fertiliser problems before the agricultural chemist are those associated with nitrogenous fertilisers and basic slag.

Nitrogenous Fertilisers.

One of the most striking developments of the war was the enormous expansion of plant for the fixation of gaseous nitrogen. It was widely supposed that the end of the war would have seen a gigantic output of nitrogenous manures which would require for their absorption considerable propaganda work among farmers. Up to the present nothing of the sort has happened, and those interested in the old-established nitrate of soda and sulphate of ammonia still retain their equanimity. And yet it seems very difficult to suppose that the war time efforts will have no counterpart in the peace period. Before the war there was no great amount of nitrogen fixation actually being carried on, but to-day all the arge civilised countries of Europe have extensive plant. An excellent summary of the position is contained in the Report of the Nitrogen Products Committee.[1]

The total possible output of combined nitrogen from existing plants in Germany alone is put at 500,000 tons, of which 60% could be produced by the Haber-Bosch process, 20% by the cyanamide process, and 20% by the gas and coke industries.[2]

This total amount is equivalent to 2½ million tons of sulphate of ammonia, which is nearly double the pre-war consumption of the whole world. The factories, however, are not working at their full capacity as yet, and nothing like this amount is being produced.

The British plant is also extensive, so also is that of France, Norway, Sweden, and Italy: whatever ills may be in store for us, we appear to be safe from the nitrogen starvation that frightened our fathers in the late 'nineties. There is, however, no occasion to fear a glut: the farmers are increasing their demands and using more nitrogen than ever, while experts consider that the limit is not yet nearly reached.

The most important groups of artificial nitrogenous fertilisers are nitrates and ammonium compounds. They have been discussed from the agricultural point of view by E. J. Russell.[3] Nitrate of lime has on an average proved as effective a fertiliser as nitrate of soda, though in special conditions the advantage lies sometimes with the one and sometimes with the other. Nitrate of ammonia is also highly effective, but it suffers from the disadvantage of being somewhat deliquescent: this is said, however, to be overcome by admixture with bone meal.[4]

Ammonium salts will apparently be produced synthetically in larger quantities than any others. On theoretical grounds the best of these as fertiliser would be the carbonate, but it suffers from the drawback that it is volatile and easily decomposable. A stable and odourless form of the bicarbonate is said to be obtainable by treating the carefully dried salt with moist carbon dioxide under 2 or 3 atmospheres' pressure.[5]

From the financial point of view the cheapest ammonium salt to prepare would apparently be the chloride, and field experiments are to be instituted to find out how it compares with other salts.

The sulphate is, however, much the commonest ammonium salt, and it is firmly established in farm practice. During the war there was a tendency for gas or coke works to produce ammonia liquor instead of ammonium sulphate, but we learn from the Alkali Inspector's report[6] that the reversion to the manufacture of the sulphate is proceeding and that the satisfactory production was attained equivalent to 397,513 tons of sulphate (24·5% ammonia, the usual basis for computation). Before the war the production was rising: it reached 388,000 tons in 1912 and 432,600 in 1913. There is more tendency than before to produce a high-grade neutral sulphate. Objection has been taken on the score that iron compounds may become converted into oxide, but there is not the slightest reason to suppose that the small amount of iron is of any value, and in field trials it has been shown that the addition of iron oxide to fertilisers failed to increase crops.[7]

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[1] Cmd. 482, 1920; see *J.*, 1920, 25R.

[2] *Z. angew. Chem.*, Dec. 19, 1919; *J.*, 1920, 59R.

[3] *J. Minis. Agric.*, 1919, **26**, 713; *cf. J.*, 1920, 5R.

[4] J. R. Partington and L. H. Parker, E.P. 151,024; *J.*, 1920, 759A.

[5] G.P. 313,827; *J.*, 1920, 22A.

In some ways the manufacture of calcium cyanamide, commonly called nitrolim in this country, is easier than other processes, and there has been great expansion of plant during the war. In 1913 the total capacity of the world's plant was 157,000 tons: in 1916 it was 981,000 tons, and to-day it is probably greater. The output capacity of German factories is estimated, as during the war, at about 600,000 metric tons per annum (about 100,000 tons of nitrogen): owing to lack of coal, etc., however, only half this production was expected during 1920.[8]

In a summary of the field trials with these various nitrogenous fertilisers it is shown that their order of effectiveness is: Nitric nitrogen 100, ammoniacal nitrogen 97, cyanamide nitrogen 90 or less. These figures are averages and include special cases where the fertilisers have a specially high or a specially low value, detailed knowledge of which would be necessary to the expert in advising in any particular instance.[9]

The relative position of cyanamide arises from the fact that it has to undergo a preliminary decomposition in the soil into ammonia, the mechanism of the change not being quite clear. G. A. Cowie has shown[10] that it is not brought about by micro-organisms, but by some chemical constituent of the soil, possibly a complex silicate. A full understanding of this change would probably improve the relative position of cyanamide by showing the types of soil to which it is not appropriate and to which therefore it should not in fairness be applied. In practice the difficulty can be diminished, if not entirely obviated, by applying the nitrolim to the soil at or before the time of sowing, and not using it as a top dressing. Experts have all along taken this view, though war time necessitated some deviations in Continental practice.[11] In addition to this fundamental difficulty there are two others which ought not to prove insuperable.

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[6] *46th Ann. Rept. on Alkali &c. Works*, 1919; *J.*, 1920, 276R.

[7] O. Lemmermann and A. Einecke, *Mitt. deuts. landw. Ges.*, 1918, **33**, 574; ., 1920, 75A.

[8] *Z. für Sauerstoff u. Stick. Ind.*, Aug., 1920; *J.*, 1920, 382R.

[9] E. J. Russell, *J.*, 1920, 5R.

[10] *J. Agric. Sci.*, 1920, **10**, 163; *J.*, 1920, 606A.

As at present manufactured cyanamide suffers from the drawback that it is both dusty and corrosive. The trouble is attributed to the presence of free lime and unchanged calcium carbide. Many efforts at improvement have been made, and recently the Prussian Ministry of Agriculture offered a prize for the best suggestion, but none was considered wholly satisfactory. The most promising is considered to be the addition of 3–4% of heavy tar-oil, which overcomes the dustiness but not the caustic action.[12]

The second disadvantage attending the use of cyanamide is that in presence of alkali, *e.g.* calcium hydroxide produced when the fertiliser becomes moist, it gives rise to a certain proportion of dicyanodiamide. Unfortunately this substance is toxic to plants and produces characteristic white tips in the leaves; further it does not readily disappear from clay or sandy soils, although in peaty soils it appears to be absorbed and apparently decomposed.[13] It has been suggested that these difficulties might be obviated by converting the cyanamide into ammonium chloride and using this as fertiliser.[14]

Phosphates.

Phosphates are of equal importance with nitrogen compounds as fertilisers, and problems associated with them are a constant preoccupation of agricultural chemists. The two great sources of supply are basic slag and mineral phosphates, formerly used entirely as superphosphate but now attracting attention for direct application to the land.

Agricultural chemists have made a close study of the old Bessemer basic slag, and it came as a considerable shock to them to find that their experiments were rendered nugatory by the disappearance of the Bessemer slag and the substitution of open-hearth slags. Further difficulties have been introduced by the circumstances that the open-hearth slags fall into two classes which at first were regarded as widely different, though fuller knowledge is rather reducing the apparent diversity. Slags made without the use of fluorspar are readily soluble in dilute citric acid solution, while those for which it is used are less soluble. It has sometimes been supposed on purely general grounds that a more soluble slag must necessarily be more effective as a fertiliser. Experiments in Essex by G. Scott Robertson show that there is a difference in favour of the more soluble slag, but it is much less than the analytical figures suggest.

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[11] H. Kappen, *Wien. landwirts. Zeit.*, 1919, **69**, 666.

[12] N. Caro, *Chem.-Zeit.*, 1920, **44**, 53; *J.*, 1920, 200A; *Chem. Ind.*, May 26, 1920; *J.*, 1920, 360R. For the physiological effects of dusty cyanamide on the workers see Siebner, *Chem.-Zeit.*, 1920, **44**, 369; *J.*, 1920, 498A.

[13] E. Linter, *Bied. Zentr.*, 1919, **48**, 414; *J.*, 1920, 166A.

[14] J. Baumann, *Chem.-Zeit.*, 1920, **44**, 158; *J.*, 1920, 275A.

The problem is very important, and it was discussed in its various aspects at a meeting of the Faraday Society held on March 23rd last, a report of which has recently been published. A committee of slag makers and agriculturists has also been set up by the Ministry of Agriculture to go fully into the question.

Meanwhile the farmers' demand for slag has been so great that it could not be met, and men have had to go short against their wish. In consequence there has arisen an enquiry into the value of mineral phosphates as manure. As already stated, mineral phosphates have hitherto been regarded in this country as raw materials for making superphosphate; but in France, the United States, and elsewhere they have been regarded as direct fertilisers and applied to the land without any preliminary treatment except grinding. In Scotland also their value has been recognised. In Robertson's experiments in Essex they proved distinctly useful on grassland, being little, if anything, inferior to basic slags. There seems, therefore, emphatically a case for further trial.

Whether they are to be used direct or first converted into superphosphate, however, it is imperative that adequate supplies should be available. Hitherto the chief sources have been North Africa and the United States; it now appears that some of the Pacific Islands (Oceania) are also more heavily stocked than was realised. Enormous deposits are reported from Nauru Island amounting to 100,000,000 tons; there are said to be 30,000,000 tons in Makatea Island, and smaller but still large quantities on many of the others.[15]

Some attention is also now being given to iron phosphates which were formerly regarded as unimportant from the fertiliser standpoint; recent experiments suggest that this opinion may require modification. A deposit in South Africa has been found to contain from 5·7 to 32·7% P_2O_5, 2·6 to 12% Fe_2O_3, and 2·2 to 17·3% Al_2O_3. Assuming this itself has but little fertiliser value, it can be converted into a citric-soluble phosphate by heating with limestone.[16]

Potassic Fertilisers.

Potassium salts are fully as necessary to plant growth as nitrogen compounds or phosphates, but in ordinary systems of husbandry they are kept circulating on the farm and are so little liable to loss that no great amount of replacement is necessary. This arises from the circumstance that the potassium mainly occurs in the straw and not in the grain, and in general the straw is kept on the farm and returned to the land in the farmyard manure.

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[15] *Bd. of Trade J.*, Dec. 18, 1919; *J.*, 1920, 41R.

[16] G. H. Stanley, *J. S. Afr. Assoc. Anal. Chem.*, 1920, **3**, 13; *J.*, 1920, **344A**.

Potash manuring is therefore not very general in ordinary farm practice. There are, however, many special kinds of farming in which the cycle is broken: in some cases the straw is sold, sometimes wool (which is rich in potash) is produced in quantity, sometimes crops particularly needing potash (*e.g.* potatoes and mangolds) are grown to a great extent. In all these cases potash manuring is essential. Potash is also important in glass-house practice.

Before the war potassic fertilisers came entirely from Germany, and few chemists had seriously considered what would happen if these supplies were cut off. Fortunately when the war came there were sufficient stocks for more than one year, so that time was given for looking round and developing other supplies. These were discussed in a previous report.

Now that the war is over there is a general reluctance to become once more wholly dependent on Germany for potash supplies. Considerable importance therefore attaches to some of the other possibilities, and at present it appears that the post-war agriculturists will draw potash from three sources:—

1. From Stassfurt in Germany, as before the war.
2. From Alsace, a recent development.
3. From such national wartime enterprises as survive into the post-war period.

1. *The German sources.*—The Stassfurt salts are so well known that no description need be given. During and since the war, however, the industry has been much disorganised, and supplies are far from being normal. During 1919 the German production was 860,000 tons of pure potash, which is much below pre-war output and less even than the normal home demand. The fault is attributed to lack of transport; the abandonment of the 8-hours day and of time wages is recommended.[17] Part of the blame also is laid on Government control.

It is said, however, that the industry is now reorganised on the basis of self-administration, and that a resumption of pre-war activities may be shortly expected[18]

2. *The Alsace deposits.*—Since the armistice these deposits have been strenuously developed. They differ in one important respect from the German: they consist mainly of chlorides, while the Stassfurt deposits contain sulphates as well. Full advantage has been taken of the temporary German disorganisation by the Alsace authorities to develop their mines. The estimated production is[19]:—

	Crude salts. Tons.	Pure potash. Tons.
1920	1,320,000	220,000
1921	2,040,000	340,000
1922	2,340,000	390,000

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[17] *Chem. Ind.*, Feb. 5, 1920; *J.*, 1920, 132R.

[18] *U.S. Com. Rep.*, May 28, 1920; *J.*, 1920, 274R.

[19] *U.S. Com. Rep.*, Feb. 20, 1920; *J.*, 1920, 132R.

Since the armistice up to February, 1920, Germany had supplied this country with only about half as much potassic salts by weight as came from Alsace (19,280 tons against 37,258 tons), though by reason of their greater richness the value was higher (£323,727 against £275,476).[20]

It is considered probable that the new kingdom of Poland will possess potash deposits, but whether they will prove of more than local importance is not yet clear.[21]

3. *Survivors of new industries.*—It is not to be expected that all the potash industries started during the war will survive, but serious efforts are being made to maintain at least one of the United States' efforts—the development of certain natural deposits—in an efficient condition, and the outlook is considered reassuring. The Searles Lake deposit at Utah, from which great results were expected, has given disappointing results, but these have now been traced to the presence of borax, which can fortunately be removed.[22]

Other Fertilisers. Organic Manures.

In addition to the usual artificial fertilisers, agricultural chemists are constantly seeking new substances having manurial value, and for long have hoped that the fertilising constituents of sewage might in some way be made available for farmers. Hitherto this has seemed impossible.

The development of the activated sludge process, however, has aroused hopes that the problem may be near solution. E. Ardern describes this process in detail and shows that 1,000,000 galls. of sewage yields no less than 1346 lb. of dry sludge containing 6·4% of nitrogen and 3·8% of phosphate: this sludge has caused considerable increase in yield of wheat.[23]

Further preliminary experiments on its fertilising value are reported by W. E. Brenchley and E. H. Richards.[24] In a sample of sludge containing 7% of nitrogen, 3·8% of phosphoric acid, and 1·1% of potash, no less than three quarters of the nitrogen was readily nitrifiable in soil and marked increases were obtained by using it in pot experiments on barley and mustard. Slate-bed sludge proved to be less effective, though it was more useful than the ordinary septic tank material, which is almost worthless.

There is a long-established prejudice in favour of organic forms of manure over the ordinary sulphate of ammonia or nitrate of soda, in consequence of which they invariably command higher prices. It has been shown at Rothamsted that these organic substances are in no sense more, but actually rather less effective than the ordinary artificials in spite of their higher price: they have, however, the great merit of freedom from harmful effects if improperly used. A long series of experiments made by J. G. Lipman and A. W. Blair,[25] at the New Jersey Experimental Station, which has just been summarised confirms this superiority of the artificial fertilisers, and the results are so important that they are given in the following short table:—

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[20] *J.*, 1920, 100R.

[21] *Chem. Ind.*, Oct. 6, 1920; *J.*, 1920, 400R.

[22] *Chem. and Met. Eng.*, Sept. 29, 1920; *J.*, 1920, 356R.

[23] *J.*, 1920, 60T.

[24] *J.*, 1920, 177T.

	Average yield of dry matter.				Nitrogen recovered. %			
	Unlimed.		Limed.		Unlimed.		Limed.	
	1908-12	1913-17	1908-12	1913-17	1908-12	1913-17	1908-12	1913-17
	lb.	lb.	lb.	lb.	%	%	%	%
Average of four artificials—								
Grain ..	6002	3631	6380	4211				
Straw, &c. ..	14,686	11,715	15,535	13,280	40·1	29·4	49·0	33·3
Average of three organic materials—								
Grain ..	5603	3467	6075	4062				
Straw, &c. ..	13,503	10,812	12,597	11,253	27·3	24·0	29·0	27·1

The artificials were nitrate of soda, nitrate of lime, sulphate of ammonia, nitrolim; the organic manures were dried blood, fish, and tankage.

A similar long series of experiments carried out at Ohio under Director C. E. Thorne, has been summarised.[26] The results for the 16 years 1903–18 are as follows:—

Unlimed land.

Crop.	Nitrate of soda.	Sulphate of ammonia.	Tankage.	Nitrate of potash.
	Plot 8.	Plot 16.	Plot 18.	Plot 22.
Tobacco (lb.) ..	1227	1095	960	1131
Wheat (bush.) ..	26·63	25·82	26·16	25·15
Clover (lb.) ..	4416	4149	4360	3987
Annual values* ..	$93·82	$85·79	$79·97	$86·61
	Limed land.			
	Plot 26.	Plot 28.	Plot 29.	
Tobacco (lb.) ..	1069	1082	959	
Wheat (bush.) ..	27·78	28·05	23·96	
Clover (lb.) ..	4139	4193	2054	
Annual values ..	$85·77	$86·78	$77·44	

* Rating tobacco at 15 cts. per lb., wheat at $2·00 per bush., and hay at $20·00 per ton.

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[25] *Soil Sci.*, 1920, **9**, 371; *J.*, 1920, 553A.

[26] C. E. Thorne, *Soil. Sci.*, 1920, **9**, 487; *J.*, 1920, 667A.

An entirely new type of method for improving crop growth has been proposed. It is not usual to think of carbon dioxide as a fertiliser, but in point of fact it is the direct cause of a large proportion of the yield of the crop and there is reason for supposing that within limits crop growth is proportional to the amount of carbon dioxide present in the atmosphere. A process has been patented in which waste gases from blast-furnaces etc. are purified from dust, soot, oil, tar, and sulphur compounds, and then led into the air in the neighbourhood of plants.[27] In glass-house experiments the concentration was maintained at about 0·5%, which is found to be the maximum permissible. Tomatoes were said to be increased 2¾ times and cucumbers 1¾ times. Even in the open air it was possible to obtain increases by discharging exhaust gases at ground level through a network of perforated pipes. Further developments will be watched with interest.

Supposed Stimulants to Plant Growth.

Persistent claims have been put forward in recent years that plant growth could be increased by the use of certain stimulants which would allow full advantage to be taken of nutrient salts or other favourable conditions present. The methods fall into two groups dealing respectively with the seed and the growing plant.

Seed treatment.—It has long been known that germination could be hastened and seedling growth improved by preliminary treatment of the seeds with certain substances, but it has not been clear that the final growth of the plant was affected except in cases where fungus spores were concerned. A treatment known as the 'Wolfryn process' has been brought out which comprises soaking and electrolysis in a salt solution and subsequent drying, and is claimed to increase final yields. No satisfactory confirmation of this claim could, however, be obtained.[28] An exception must apparently be made of infected seeds, where heating has been shown to be a feasible treatment, as the seeds will withstand temperatures fatal to the fungus.[29]

The growing plant.—Bottomley supposes that plants, like animals, need "vitamines," and that if such substances are supplied further growth can be obtained. He maintains that bacterised peat and growth products of *Azotobacter* and of *B. radicicola* have the effect of stimulating the water weed, *Lemna minor*.[30] Even if this were true of *Lemna*, it by no means follows that it holds for higher plants also. There is, however, experimental evidence that citrus seedlings were benefited by dilute solutions of peat extracts,[31] and there is also the possibility that farmyard manure may act in some special way.[32]

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[27] F. Riedel, G.P. 312,793; *J.*, 1920, 667A; *Stahl u. Eisen*, 1919, **39**, 1497; *J.*, 1920, 125A. See also M. B. Cummings and C. H. Jones, *Special Bull.* 1919.

[28] E. J. Russell, *J. Min. Agric.*, 1920, **26**, 971; *J.*, 1920, 201A.

[29] D. Atanasoff and A. G. Johnson, *J. Agric. Res.*, 1920, **18**, 379; *J.*, 1920, 243A.

[30] W. B. Bottomley, *Proc. Roy. Soc.*, 1920, **91** B, 83; *J.*, 1920, 200A.

The effect of overhead electrical discharge on plant growth is still being investigated: it is more promising than either of the foregoing methods in that it does appear to increase plant growth. There is not yet sufficient evidence to show whether the method is economically sound.

SOILS.

From the point of view of the practical agricultural chemist concerned with applications rather than fundamental investigations the most important recent work has been that on sourness and acidity in soil. Both subject and methods are still in a state of considerable flux, and it will probably be more convenient for the reader to have a connected account of the points of the various papers.[33]

Agricultural chemists have long been accustomed to estimate the amount of lime or of carbonate in a soil with a view to finding whether there was a sufficient amount to act as a margin of safety. If small quantities only were present, or if the soil were acid, they advised that more lime should be added, but usually did not specify a precise quantity, leaving that question to the farmer to decide. In recent years, however, they have aspired to do more than this, and have attempted to tell the farmer exactly what quantities he ought to use. In the case of acid soils the method has been essentially a titration; lime or calcium bicarbonate has been added in known quantity, and the excess above the neutral point has been determined: the quantity required to obtain neutrality is called the "lime requirement." In America Veitch's is the common method,[34] in England Hutchinson and McLennan's has been used.[35]

It now appears, however, that the disappearance of lime or of calcium bicarbonate is not entirely due to neutralisation of an acid, but is also partly a physical sorption effect. There is no sharp end-point: the quantity absorbed depends on the quantity added. A curve of the ordinary adsorption type is obtained: there is no particular definite lime requirement. Under strictly similar conditions one soil may be compared with another, and may be said to require more or less lime to ensure satisfactory crop conditions, and if the analyst has a sufficiency of field results he can make corrections in his analytical data and draw up an empirical scale of lime requirements that will on the whole give useful information. From the practical point of view this has proved satisfactory.

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[31] J. F. Breazeale, *J. Agric. Res.*, 1919, **18**, 267.

[32] F. A. Mockeridge, *Biochem. J.*, 1920, **14**, 432; *J.*, 1920, 606A.

[33] The papers are very numerous. Among them are:—H. C. Knight, *J. Ind. Eng. Chem.*, 1920, **12**, 457, 559; *J.*, 1920, 523A, 578A; A. W. Blair and A. L. Prince, *Soil Sci.*, 1920, **9**, 253; *J.*, 1920, 523A; J. S. Joffe, *Soil Sci.*, 1920, **9**, 261; *J.*, 1920, 523A; E. Truog and M. R. Meacham, *Soil Sci.*, 1919, **7**, 469; *J.*, 1920, 200A; J. W. M. Bunker, *J. Biol. Chem.*, 1920, **41**, 11; *J.*, 1920, 249A; E. T. Wherry, *J. Wash. Acad. Sci.*, 1920, **10**, 217; *J.*, 1920, 419A.

[34] *J. Amer. Chem. Soc.*, 1902, **24**, 1120.

[35] *J. Agric. Sci.*, 1915, **7**, 75.

Agricultural chemists have, however, attempted to go still further. They have shown that the effect of lime is not simply to neutralise acids: it directly benefits the plants, improves the physical condition of the soil, throws out of action aluminium or iron salts which may assume importance and cause injury to plants, and restores the absorption relationships of the soil to their normal character. Obviously it is important to make a closer analysis of the problem so as to determine for any given soil type the precise function of the lime.

At present attention is being confined to soil acidity on which numerous investigations are being made. A special nomenclature is used so as to bring the work into line with some of the modern developments of biological chemistry. As this differs from the nomenclature in common use among chemists some account of it will be given: fundamentally it is open to objection, but it has the merit of conciseness and simplicity of appearance.

Acidity is studied in two ways:—

1. By measuring the hydrogen ion concentration.

2. By determining the titration value, *i.e.*, the number of c.c. of standard alkali solution which a given volume of the acid solution will neutralise. In the language of the dissociation hypothesis this value measures the total quantity of hydrogen ions producible under the conditions of the experiment, supposing them to be neutralised or linked up with -OH ions as quickly as they are liberated.

The titration value measures the quantity of the acid, but it makes no distinction between a strong acid, such as sulphuric acid, and a weak acid, such as acetic acid: the great difference in action on plant life exhibited by the two acids is missed altogether. Moreover the titration value is not an absolute constant: polybasic acids, which are by far the most numerous, have several titration values, according as to whether one, two, or more of the hydrogen ions are affected. Different indicators therefore give different results. So long as the constitution of the acid is known this does not matter, but it causes complications in dealing with a mixture of unknown acids.

Many of the methods suggested for measuring soil acidity, including all the "lime requirement" methods, afford a more or less rough measure of the titration value: the differences in the results are partly due to absorption and partly to the differences in the number of the hydrogen atoms concerned.

The determination of the concentration of hydrogen ions, *i.e.*, of the ions actually present, as distinct from those that would finally be liberated on neutralisation, is an attempt to measure the intensity of the acid as distinct from its quantity. The principle of the method is simple in dealing with solutions of pure acids: it is based on the ordinary dissociation law:—

$H \times X \div HX = K$, where H and X are the ions produced on the dissociation of the acid HX, and K is a constant. The number or the concentration of the ions is measured by the electrical conductivity of the solution, but once this has been determined for a given acid it can become a standard against which the hydrogen ion concentrations of other acids can be rapidly compared by means of a set of indicators.[36]

The problem becomes more complex when salts are present, because the additional ions thus introduced affect the amount of dissociation: in particular they make it difficult for the hydrogen ion concentration to increase when another acid is added. Colloidal substances act in the same way. This effect, known as the "buffer action," is of great importance in vital phenomena, and is well marked in the case of soils. Thus if an acid is added to soil the increase in the hydrogen ion concentration is not nearly so great as if the same quantity of acid were added to water.[37]

The numerical values of the hydrogen ion concentrations are rather unmanageable, and a convention has therefore been adopted in dealing with them.

In pure water or a neutral solution $H^{\cdot} = OH' = 1 \times 10^{-7\cdot07}$ gram of H ions per litre.

Acidity means a hydrogen ion concentration in excess of that of water, *i.e.*, the index instead of being –7·0 is greater: as the quantity is negative this means that the number itself is less: it may fall to zero. Simple trial will show that it is very difficult to plot on the same curve numbers ranging from 1 to 1×10^{-7}. A further complication began to arise, but fortunately was checked: investigators expressed their results in terms not of 1, but of some other number, multiplied by 10 to some negative power, *e.g.*, one solution might be represented by the value $4{\cdot}4 \times 10^{-6}$, and another by $6{\cdot}8 \times 10^{-7}$, and it was difficult to make a comparison.[38]

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[36] A useful account of the measurement of the hydrogen ion concentration is given by J. F. McClendon in "Physical Chemistry of Vital Phenomena" (1917), which was written for biological students.

[37] For a critical summary of recent work see E. A. Fisher, *J. Agric. Sci.* 1921, **11**, 19.

To overcome the first of these difficulties S. P. L. Sörensen adopted the familiar device of plotting the logarithms of the numbers instead of the numbers themselves; and to overcome the second he reduced all to terms of $1 \times$ some power of 10: thus the two cases quoted above become $10^{-5{\cdot}36}$ and $1 \times 10^{-6{\cdot}17}$ respectively He calls the numbers 5·36 and 6·17 the p_H values of the solutions; in reality they are the values for the $-\log$ (H·). On this notation the p_H value for neutrality is 7·07; that for acidity is anything less—down to nothing—that for alkalinity is anything greater up to 14·14.

In consequence of the buffer action already mentioned these values are not liable to disturbance by small additions of substances to the soil.

A large number of determinations of the p_H or $-\log$ (H·) values for American soils have been made by L. J. Gillespie[39] and L. T. Sharp and D. R. Hoagland,[40] while for British soils a beginning has been made in the Rothamsted laboratories. Some of the values are as follows:—

	Sharp and Hoagland.	British soils.
Acid soils, extreme value	3·7	4·4
Fertile soils	7·04—7·52	7
Alkaline soils, extreme value ..	9·7	

The acidity of the root sap is of the order of 5 or 6.[41]

The relatively small range of variation in comparison with the large variation in amount of titratable acidity is explained by the buffer action described above.

Insecticides and Partial Sterilising Agents.

Intensive culture is attended with the drawback that it encourages a multitude of disease organisms which the agricultural chemist is now seeking to control. Two methods are used: heating, which is very effective but costly and limited in its application, and chemical treatment, which offers the prospect of cheapness and practicability, although it is turning out more difficult than was expected.

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[38] *Biochem. Zeits.*, 1909, **21**, 130; **22**, 352; see also "Ergebnisse d. Physiologie" (Asher and Spiro), 1912, **12**, 393.

[39] L. J. Gillespie and L. A. Hurst, *Soil Sci.*, 1917, **4**, 313; and L. Wise *Amer. Chem. Soc.*, 1918, **40**, 796.

[40] *J. Agric. Res.*, 1918, **12**, 139.

[41] C. B. Clevenger, *Soil Sci.*, 1919, **8**, 217; *J.*, 1920, 249A.

Of the various chemicals empirically tested sodium cyanide has proved useful in certain cases: 165 lb. dissolved in 12,000 galls. of water and sprayed over an acre of land kept in check the grubs of certain beetles, chiefly *Popillia japonica*, without permanently injuring the crop. The cyanide disappeared from the soil in seven to ten days, and the addition of ammonium sulphate accelerated its disappearance.[42]

Chloropicrin has been found effective in destroying white ants when used at the rate of 2–5 mg. per litre of air, and it was immaterial whether the ants were freely exposed or in fragments of wood 10 cm. thick.[43]

It may be doubted, however, whether the empirical method will carry the problem far towards solution. A more promising method seems to be the systematic study of the relationship between chemical composition and toxicity to the various groups of organisms concerned. This is being adopted at Rothamsted.

Industrial Crops.

In general the British farmer is not interested in industrial crops, most of his produce being converted into milk or meat on the farm, or sold as grain to the miller. There would, however, be obvious advantages in bringing fresh sources of revenue into agriculture and serious attention is being paid to the possibility of introducing such crops into the scheme of British farming: sugar beet is a well-known instance.

An interesting example is furnished by Captain A. P. H. Desborough,[44] who is investigating the possibility of producing alcohol from crops. On an average 120 galls. of alcohol is obtainable from 1 ton of fermentable carbohydrates and, as the alcohol must be retailed at 3s. 2d. per gall. in order to compete with existing supplies, and as retailing will cost 1s., manufacture 9d., interest on capital 4d., there remains only 1s. 1d. to pay for raw material, which allows £6 10s. per ton of pure fermentable carbohydrate. In order to supply at this price the maximum price payable for crops would be: Mangolds 11s., potatoes 23s., Jerusalem artichokes 23s. These prices are considerably before those now obtainable: at the moment of writing mangolds are being sold at £3 per ton and potatoes at £10. It is possible, however, that artichokes[45] might be producible at 23s. per ton or that some other vigorous growing crop might prove better.

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[42] J. J. Davis, *Soil Sci.*, 1920, **10**, 61; *J.*, 1920, 699A.

[43] J. Feytaud, *Comptes rend.*, 1920, **171**, 440; *J.*, 1920, 671A.

[44] *British Ass. Repts.*, 1920; *J.*, 1920, 30R.

[45] For production of alcohol from artichokes see also M. Rüdiger, *Z. Spiritusind.*, 1920, **43**, 203; *J.*, 1920, 608A.

Wheat.—It is well recognised that some wheats known as "strong" wheats produce large, well-shaped leaves, while others, the "weak" wheats, produce only small, squat-looking leaves. Many attempts have been made to correlate this property with various chemical and physical characteristics of the grain, and F. J. Martin finds, in partial confirmation of previous workers, that strong wheats possess a minimum gas-producing but maximum gas-retaining capacity and high gliadin content. No relation could be found, however, between strength and the amounts of total soluble extract, soluble phosphorus, and acidity.[46] The agricultural interest in the problem lies in the fact that British grown wheats are generally weak, while Canadian wheats of the Red Fife type are usually strong and therefore command a rather higher price.

Indigo.—Special interest attaches to indigo in India as being the last surviving of the dye crops. During the war years there was a great increase in the area planted with indigo, as the exclusion of the synthetic product from the world's markets gave the natural substance a monopoly, but the area has now fallen to pre-war dimensions.[47] Whether it will be possible to improve the yield per acre and so to increase total output in spite of the reduction in acreage remains to be seen. The yield can be increased by the use of superphosphate as fertiliser: the proportion of indican also increases under this treatment.[48]

FEEDING.

The conventional method of examining feeding stuffs in agricultural laboratories goes back to the 'sixties, and is based on an animal physiology that is now largely abandoned. Agricultural chemists of sufficient experience are able to make useful practical deductions from the results, but the method is of little assistance to the investigator of farm crops.

One of the worst defects is that a large part of the material usually called nitrogen-free extract but sometimes called carbohydrates, is obtained by difference. This gives a specious appearance of accuracy to the analyses, but it has the disadvantage that much of the feeding stuff is not examined at all. Of recent years several investigations on this group have been made, and A. J. W Hornby now reports the results of his studies of the pectins.[4] Methyl pectate forms from 10 to 20% of the dry matter of beets carrots, parsnips: it is suggested that this substance, in addition to its feeding value to animals, may confer on the plant con

[46] *J.*, 1920, 246T.

[47] *Indian Trade J.*, Oct. 22, 1920; *J.*, 1920, 398R.

[48] W. A. Davis, *Indigo Publ. No.* 4, 1918, *Pusa*; *J.*, 1919, 248A.

[49] *J.*, 1920, 246T.

siderable protection against the attacks of insect pests since the digestive juices would readily produce methyl alcohol from it.

Considerable quantities of nitrogen-free extract occur in straw, and it is suggested that sugar is an important constituent, accounting for some of the marked differences in nutritive value observed in different samples of straw. The nutritive value is known to vary with the locality, and to be higher in the north than in the south. Analysis shows[50] that a sample of oat-straw in the north contained 5·6% of total sugar, while one from the Midlands contained 5·0% and a stored sample contained none.

A further difficulty about the conventional method is that it completely ignores harmful constituents such as the hydrocyanic acid generated from glucosides. It is now well known that beans of *Phaseolus lunatus* come within this category.[51] Sudan grass (*Andropogon Sorghum* var.) has also to be added to the list of crops readily yielding hydrocyanic acid and therefore liable to injure cattle. It was found to yield about one-third as much as did the grain sorghums: the quantity is greatest in the young plant and decreases as growth continues.[52]

A more serious defect of the method is that it takes account of only a few groups of constituents.

It is now generally recognised that the old groups of nutrient substances are insufficient entirely to characterise a feeding stuff; it is necessary, also, to have regard to the accessory bodies or vitamines present without which animals cannot grow. Three types of vitamines are now recognised:—

1. Fat-soluble A, which is associated with animal fats, particularly butter and cod liver oil, but not lard or vegetable fats; it is also present in green leaves and embryos of seeds.
2. Water-soluble B, associated with embryo and bran of cereals, seeds of pulses, eggs, yeast, and vegetables; this is identical with the anti-beriberi vitamine of the earlier workers.
3. The anti-scorbutic factor, not essential to growth though necessary for maximum growth.[53]

T. B. Osborne, whose work on the proteins of farm crops is favourably known to agricultural chemists, is now turning his attention to the vitamines of farm foods and has already made some interesting additions to our knowledge. He shows that lucerne and clover are extraordinarily rich in water-soluble B. Timothy hay, however, is not. Turnips and cabbage contain less than lucerne and clover, as also do vegetables such as spinach, carrots, and beetroot used for human rather than animal consumption. Potatoes, however, are well supplied.[54]

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[50] S. H. Collins and A. Spiller, *J.*, 1920, 66T.

[51] H. Lührig, *Chem.-Zeit.*, 1920, **44**, 166; *J.*, 1920, 277A.

[52] P. Menaul and C. T. Dowell, *J. Agric. Res.*, 1920, **18**, 447; *J.*, 1920, 277A.

[53] For a full account of the present position of this subject see *Special Report Series No.* 38, *Medical Research Com., London*; *J.*, 1920, 42R.

From the human point of view another paper by the same authors is interesting. It is shown that fresh juices of orange, lemon, and grape fruit are also rich in water-soluble B, being as effective as an equal volume of cows' milk.[55] The fat-soluble A is extractable by alcohol from various farm foods. Lucerne and clover are rich in this constituent also, as are timothy and spinach: cabbage, however, contains less.[56]

Studies are reported of this vitamine as prepared from cabbage and carrots.[57] It also occurs in the maize kernel, where it is said to be intimately associated with the yellow pigment.[58]

The year's work on vitamines is dealt with more fully in the section on "Foods."

Straw as food.—It has always been one of the troubles of the agricultural chemist that so little effect could be obtained from straw as food. Although cellulose is a carbohydrate it has nothing like the value of sugar. During the war serious attempts were made in Germany to treat straw with some agent that would hydrolyse the cellulose and convert it into something of greater nutritive value. Examination by W. Godden suggests little hope for these methods under normal English conditions.[59] One of the best of them consisted in treatment of straw with sodium hydroxide. This certainly improved the feeding qualities of the straw, nearly doubling its value for production purposes and adding 50% to its value for maintenance purposes. Whether the process is economical, however, can obviously be ascertained only after large-scale trials have been made. Other methods have also been suggested: whatever their practical value they remain as interesting applications of chemistry to the difficult wartime problems of Central Europe.

In one method patented in Germany for the preparation of animal food from wood, straw, etc., the wood is treated with alkali and chlorine,[60] the straw with alkali or with calcium saccharate.[61] In another process the straw is digested with sulphuric acid, when reducing sugars are formed[62] which are said to possess considerable nutritive power.

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[54] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1920, **41**, 451.

[55] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1920, **42**, 465; *J.*, 1920, 609A.

[56] T. B. Osborne and L. B. Mendel, *J. Biol Chem.*, 1920, **41**, 549; *J.*, 1920, 422A.

[57] S. S. Zilva, *Biochem. J.*, 1920, **14**, 494; *J.*, 1920, 609A.

[58] H. Steenbock and P. W. Boutwell, *J. Biol. Chem.*, 1920, **41**, 81; *J.*, 1920, 245A.

[59] *J. Agric. Sci.*, 1920, **10**, 437; *J.*, 1920, 797A.

[60] H. Mühlenbein, G.P. 305,090; *J.*, 1920, 346A.

[61] G.P. 306,464; *J.*, 1920, 347A.

W. Godden reports a digestibility trial made with peat moss digested with hydrochloric acid, whereby it was claimed some 15–20% of reducing sugar would be formed. It was found, however, that the digestibility had only slightly increased.[63]

Simple heating of the hay, straw, etc., in a revolving drum kept at 300°–400° F. is also said to yield assimilable substances from cellulose.[64] Even if the feeding stuff obtainable by these methods contains a certain amount of carbohydrate it would then still be deficient in protein, but this defect was to be remedied in a remarkable manner, according to H. Pringsheim and S. Lichtenstein,[65] by the activity of moulds. A nonpathogenic *Aspergillus* is grown in a solution containing ammonium chloride, kainit, and superphosphate, and poured on to the straw. The fungus then assimilates the ammonia, converting it into protein.

Other investigations.—Of the numerous other investigations space allows only mention of three.

The protein of soy bean is more completely utilised by chickens than by mammals.[66]

The preparation of silage from lucerne is a difficult matter, and farmers sometimes stack the partially wilted green crop and allow it to ferment. The resulting material is said to be readily eaten by cattle, but it is produced at great loss.[67]

Successful attempts have been made to produce sunflower silage, which may prove useful in regions where maize will not grow.[68]

MILK AND DAIRY.

Now that efforts are being made to encourage the cheese industry it is important that some method of utilising whey should be discovered. Whey contains 6·5–7·5% of dissolved substances, of which 60–70% is milk sugar. It can be used direct for stock feeding, but the conditions are not always favourable, and then it can be used for the manufacture of milk sugar, of which prior to the war almost all the supplies came from the Continent. The preparation of milk sugar is not altogether simple ; small quantities of acids and salts are present in whey which convert some of the sugar into a non-crystalline variety that is easily lost, while the protein leads to frothing in the vacuum pan, retards crystallisation, and adversely affects the keeping properties of the lactose. A method has been proposed by H. E. Woodman[69] for overcoming these difficulties, the essential feature of which is that the whey is heated to a sufficient temperature to coagulate the protein, and then filtered, before proceeding to final evaporation.

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[62] F. Scurti and G. Morbelli, *Staz. Sper. Agrar. Ital.*, 1919, **52**, 238; *J.* 1920, 464A.

[63] *J. Agric. Sci.*, 1920, **10**, 457; *J.*, 1920, 797A.

[64] C. J. Coleman and H. G. Jones. E.P. 134,944; *J.*, 1920, 78A.

[65] *Chem.-Zeit.*, 1920, **91**, 414; *J.*, 1920, 733A.

[66] A. G. Philips, R. H. Carr, and D. C. Kennard, *J. Agric. Res.*, 1920, **18**, 391

[67] C. O. Swanson, L. E. Call, and S. C. Salmon, *J. Agric. Res.*, 1919, **18**, 299 *J.*, 1920, 169A.

[68] R. E. Neidig and L. E. Vance, *J. Agric. Res.*, 1919, **18**, 325; *J.*, 1920 170A.

[69] *J. Agric. Sci.*, 1920, **10**, 1 ; *J.*, 1920, 309A.

SUGARS, STARCHES, AND GUMS.

By James P. Ogilvie,

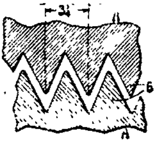
Sugars.

Statistical.—According to Willett and Gray, the 1919–20 world's crop of cane and beet sugar came to 15,222,684 tons, 11,949,747 being cane, and only 3,272,937 being beet. In both cane and beet production there was a deficiency as compared with the previous year; but in the coming year (the 1920–21 season) an increase in both kinds is predicted, especially in regard to European beet, which is expected to increase to 3,648,372 tons, as compared with 7,962,364 in 1913–14. Regarding the world's crops for 1920–21, the preliminary estimate is given by the same authority as 17,302,510 tons, of which 12,689,138 is cane and 4,613,372 is beet sugar, a total increase of fully 2 million tons over 1919–20.

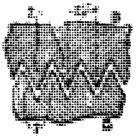
The Cane Sugar Industry.

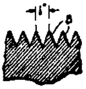
Extraction of the juice.—Increasing attention is being devoted in most countries to the treatment of the cane previous to its entry into the train of three, four, or five 3-roller mills comprising the modern crushing installation. These preparatory appliances consist of crushers, shredders, and revolving knives, which have as their purpose the splitting and levelling of the stalks, and their delivery in the form of an even mat to the first unit of the milling plant.

In regard to crushers, hitherto one 2-roller apparatus, the peripheral surface of which is provided with deep ribs, has been employed; but the combination of two is stated to have given improved results in a number of factories in Cuba.[1] As is shown in the illustration, the pitch of the ribs in the case of an

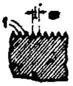


1st CRUSHER


2nd CRUSHER



1st MILL


2nd, 3rd, 4th & 5th MILLS

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[1] *Intern. Sugar J.*, 1919, 406, 471.

apparatus protected by H. Hurter[2] decreases successively in the first crusher, the second crusher, and the first mill, being least in the second, third, fourth, and fifth 3-roller mills. Such an installation is said to combine in a high degree a rapid rate of grinding and a high yield, and figures are published[3] which show an extraction value (that is, sucrose present in the juice per cent. sucrose in the cane) of 94·1 using only 7·4% of water for maceration, while working at a speed as high as 129·6 tons of cane per hour. Respecting shredders, it may be remarked that very satisfactory reports continue to be made of the work of the Searby type in Hawaii and elsewhere; while it may also be mentioned that a patent exposing details of a system of revolving knives, an improvement upon the Ramsay device, has recently been published.[4]

Clarification of the juice.—Raw cane juice as it comes from the mills is a light grey to dark green fluid. Its most important soluble impurities from the point of view of the essential stage of manufacture now about to be discussed consist of (A) the colouring matter termed "saccharetin," which originates from the fibre of the cane; (B) the pigments of the anthocyanin group, which come from the rind of the cane; and (C) the ferric-polyphenol compounds, which have recently been shown to result from the action of peroxidase on a catechol derivative,[5] the product thus formed combining with the iron dissolved from the mill rollers by the vegetable acids of the juice. Its insoluble impurities consist mainly of "cush-cush" (*i.e.*, fine particles of crushed cane, also called *bagacillo*), chlorophyll from the rind of the stalk, wax, and inert substances, as sand and clay. Lastly, mention must be made of the gums and pectins, which owing to their slimy nature unfortunately preclude the possibility of filtering the raw juice.

An ideally efficient method of clarifying such a liquid would have two results, namely: (1) the removal of the soluble colouring matters mentioned, if not entirely, at any rate to a large extent; and (2) the elimination of the troublesome gums and pectins, at least sufficiently to make filtration through cloth or other medium a practicable operation for the production of a brilliantly clear juice. It is hardly necessary to add that such a procedure should fulfil yet another condition, namely, that it should not give rise to any products capable of adversely affecting subsequent stages of manufacture, and certainly not to other colouring matters. It would seem instructive to examine our present methods of clarifying cane juice in the light of these high standards.

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[2] U.S.P. 1,339,600.

[3] *Intern. Sugar J.*, 1920, 408.

[4] U.S.P. 1,348,751.

[5] *J. Ind. Eng. Chem.*, 1918, **10**, 814; *J.*, 1918, 778A; *Ann. Repts.*, 1919, **4**, 368. Also *J. Ind. Eng. Chem.*, 1919, **11**, 1034; *J.*, 1920, 167A.

Addition of a small quantity of lime, say, to neutrality or slight alkalinity, followed by heating to boiling point—the so-called "defecation process" (always employed on account of its simplicity and economy in the production of the raw sugar destined for the refinery)—is recognised to be quite an imperfect process. It fails to eliminate the soluble colouring matter to any considerable extent, nor does it remove much of the gums and pectins; while, after subsiding as much as possible of the impurities thrown out of solution, a liquid containing a comparatively high amount of solids in suspension may result. Sulphitation, in which a moderate excess of lime is added and subsequently neutralised by sulphur dioxide, certainly has a better effect, since the juice is lighter in colour, and most of the suspended matter is carried down by the voluminous precipitate of calcium sulphite formed; but this procedure does not get rid of the gums and pectins sufficiently to make filtration feasible, and, therefore, the liquid has to be subsided. Moreover, sulphitation eliminates a part only of the anthocyanins. Carbonatation, on the other hand, in which a large excess of lime is added (7–10 times that used in sulphitation) and later is thrown down by carbon dioxide, precipitates all the anthocyanins, and such a proportion of the gums and pectins that both the juice and the syrup obtained later by concentration in the evaporators can be passed through cloth.

It is now possible to say something more of the inadequacy of defecation and sulphitation as means for the removal of the impurities from cane juice. Useful work carried out by F. W. Zerban[6] demonstrates that both these methods of clarification may under certain conditions produce juice appreciably darker in colour than before treatment. This formation of colour was shown to be due to some extent to the cause suggested last year by W. H. T. Harloff,[7] namely, the decomposition of the "glucose" (lævulose and dextrose) by the lime at a high temperature, and probably also in a less degree to the reaction occurring between the reducing sugars and amino-acids, to which attention was also drawn in the last report[8]; but it would seem from these tests that the greater proportion of colour production is due to the presence of ferric-polyphenol compounds.[9] Solutions containing some of the iron-greening tannin isolated from cane, in addition to sucrose, "glucose," asparagine and aspartic acid, were treated by different modifications of the defecation and sulphitation processes, both in the absence and in the presence of an iron salt, care being taken to make the proportion of the constituents of these artificial juices correspond as closely as possible to that in which they are present in the natural product. Examination of the clarified juices in the absence of iron showed that, although part of the tannin had been removed, the treatment had largely brought about the formation of colouring matter, probably owing to the oxidation of this tannin. Still darker juices resulted in the presence of iron, though in all the tests using sulphitation the bleaching effect of the sulphur dioxide was quite marked. Lastly, evidence was adduced showing that probably the particular iron-greening tannin which had been added to these artificial juices is not alone responsible for this serious formation of colour, but that its oxidation products, as well as the cane pigments saccharetin and anthocyanin (both of which are also polyphenol derivatives), play an important part.

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[6] *J. Ind. Eng. Chem.*, 1920, **12**, 744; *J.*, 1920, 667A.

[7] *Ann. Repts.*, 1919, **4**, 388.

[8] *Ibid.*, 1919, **4**, 382.

[9] *Ibid.*, 1919, **4**, 388.

It would, therefore, seem proven that both these methods are far from capable of fulfilling the two conditions of an ideal clarification postulated above, viz., the removal of the colouring matter and also that of the gums and pectins. Recent work has shown, however, that an improvement is likely to be effected by studying the operation of clarification in the light of colloidal chemistry, and several investigators have turned for help in this direction. Thus, H. C. Prinsen Geerligs[10] has remarked in substance that the essential result of the two most effective methods of clarification (sulphitation and carbonatation) is not so much to remove any great amount of impurities, as partly to eliminate the small amount of colloidal matter present in the juice. N. Deerr[11] has carried out experiments with cane juices showing that more than half the amount of precipitate obtained in the defecation process is originally present in the colloid state in the juice; and that filtration through asbestos under pressure (a tedious operation, quite impossible in factory practice) removes the same substances that are eliminated by heating to about 88° C. (190° F.). He further showed that only about 28% of the purifying effect in the defecation process can be considered to be due to the chemical action of the lime, the rest being attributed to the elimination of the colloids by coagulation on heating and by adsorption during setting. R. S. Norris[12] has carried out experiments on the filtration of juices through Chamberland filters, obtaining increased purities of 2·7° and 8·8° in first and last mill juices respectively, values which are much higher than those obtained by the ordinary defecation process. S. S. Peck[13] has described the colloidal nature of the most important impurities present in raw cane juice, colouring matters as well as gums and pectins, and has drawn attention to the fact that polyphenol compounds behave as typical protective colloids.

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[10] "Practical White Sugar Manufacture," pp. 62-63.

[11] *Intern. Sugar J.*, 1916, 502; *J.*, 1916, 1078.

[12] *Intern. Sugar J.*, 1919, 71.

[13] *Ibid.*, 1919, 70.

Moreover, an effort has been made to carry this conception of the colloidal nature of clarification into practice by W. H. T. Harloff,[14] who in an article written shortly before his death (which is much deplored in the industry) considered the conditions most likely to increase the adsorption of the colloids by the calcium sulphite precipitated in the sulphitation process. He described experiments demonstrating that the precipitate should be as voluminous as economic conditions will permit, and that its "porosity" is enhanced by its formation in a granular state, which is induced by preliminarily raising the temperature of the raw juice to the highest degree possible without incurring inversion (85°–90° C.), and by subsequently conducting liming and sulphiting simultaneously. An enhanced colloidal effect was also obtained by keeping the juice slightly acid during the subsiding of the calcium sulphite precipitate, it having been found that when this condition is observed settling is quite rapid, whereas when the reaction is alkaline, or even neutral, gums and pectins are not adsorbed, and subsiding becomes appreciably slower.

These results are certainly interesting, but it is doubtful whether even altogether they would lead to any very greatly improved effect in clarification. One is much rather inclined to enquire whether it would not be possible to utilise other more powerful adsorbents than the precipitates produced during sulphitation and carbonatation. At various times the effect of adding alumina, silica, clay, pumice, peat, pulp, sawdust, and different forms of carbon has been tried; but of these materials none has hitherto been regarded to be of practical value. Particularly encouraging experiments have recently been conducted, however, on the use of kieselguhr, followed by a highly active form of carbon, and for these results we are indebted again to F. W. Zerban.[15] On mixing the juice with about 0·5% of kieselguhr, and raising its temperature to boiling point, he found that filtration could be conducted without difficulty, the liquid obtained after this operation being brilliant, though not very greatly improved in colour. In order, therefore, to complete the adsorption of the colloids, it was heated with 1% of the powerful decolorising carbon known as "Norit,"[16] a water-white solution thus resulting. Analysis showed that the treatment with kieselguhr alone raised the quotient of purity (sucrose per cent. total solids) as much as sulphitation generally does, viz., about 0·4%, and that after the application of "Norit" it was increased to 2·0%. These experiments carried out in the laboratory were confirmed in large-scale operations, and it was fully proved that a white sugar, superior in quality, and not inferior in yield, compared with that in ordinary sulphitation practice, could be obtained. Another result was that the molasses, being much lighter in colour, had an appreciably higher market value as a table syrup than had that produced by the usual plantation methods.

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[14] *Archief Suikerind. Nederl.-Indië*, 1920, **28**, 802; *J.*, 1920, 828A.

[15] *Louisiana Bulletin*, No. 173; *J.*, 1921, 21A.

[16] *J.*, 1913, 85; 1914, 853; 1915, 370; 1918, 16A, 160A.

It would consequently seem that the application of kieselguhr in this way to adsorb the coarser dispersoids of the raw cane juice, followed by decolorising carbon to take up the more highly dispersed colloids, approaches very closely, so far as the chemical and physical results are concerned, to the ideal method of clarification to which reference has been made in this discussion. It is unfortunate that, at the present time at any rate, it is unlikely to be as favourably regarded from the economic point of view, since the cost of its application to practice would doubtless prove much higher than that of sulphitation and carbonatation. It appears, therefore, to be of much importance for sugar manufacturers to concentrate upon the problem of the production of cheap and efficient adsorbents of the nature described. W. D. Horne[17] remarks that what is required is " a decolorising carbon cheap enough to throw away after using once, and which will adsorb 10–20 times as much colour as bone-black with ash and organic impurities in proportion." This may be asking much ; but, bearing in mind the fact that the production of high-power decolorising carbon is still almost an innovation, it does not seem unreasonable to expect that an approach may be made towards this desideratum in the near future, possibly in the direction of discovering a by-product of powerful adsorbing capacity, capable, moreover, of being repeatedly revivified after use. Notice may now be briefly taken of some of the more important work carried out during the past year in the direction of preparing such a cheap and active adsorbent.

C. F. Bardorf,[18] on examining the high-power carbon " Eponit " microscopically, found it to be composed of charred plant tissues covered with numerous nodules of carbon. By condensing the soot resulting from the combustion of peat, he prepared a material corresponding in every way with the Austrian product ; while by mixing charred sawdust with a powerful carbon, such as " Eponit " or " Norit," he was able to obtain a material giving a better result than either of the ingredients used, this improved effect being believed to be due to the dispersion of the particles of active carbon by means of the charred sawdust. R. W. Mumford[19] has protected a method of preparing a powerful carbon by slowly heating to

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[17] *J. Ind. Eng. Chem.*, 1920, **12**, 1015.

[18] *Canad. Chem. J.*, 1920, **4**, 207 ; *J.*, 1920, 759A.

[19] E.P. 133,759 ; U.S.P. 1,287,592 ; *J.*, 1919, 129A.

250° C. an intimate mixture of moist comminuted vegetable matter (peat, sawdust, etc.), colloid material (a solution of gelatin), and mineral spacing agent (dolomite), then more rapidly raising the temperature to 800°–900° C., the mass being finally dumped into water with exclusion of air, and the mineral matter separated from the carbon as completely as possible by subsiding or centrifuging. J. N. A. Sauer,[20] in a recent patent specification relating to a method of clarifying raw cane juice, mentions that an efficient material may be prepared by heating bagasse or beet pulp with hot gases (as ammonia, carbon dioxide, carbon monoxide, chlorine, or superheated steam), though no further details are given. Two methods of revivification have been protected. In the first, A. Adams and S. S. Peck[21] allow the adsorbed impurities in the spent material to ferment by immersion in water maintained at a suitable temperature, the mass being subsequently heated with an electrolyte and washed with water; while in the second, G. Blardone[22] treats the used carbon with a solution of sulphur dioxide or a sulphite, preferably heating. Mention may be made of two patents concerning adsorbents other than decolorising carbon. J. J. Hood, J. Clark, and P. G. Clark[23] pass sugar liquor through ignited precipitated alumina, precipitated magnesia, bauxite, or mixtures of these, the material being revivified by heating to dull redness with exclusion of air; and O. Bielmann[24] adds silicic acid (prepared by treating sodium silicate with carbon dioxide) to the heated liquid, the precipitate while subsiding carrying down colloidal impurities.

Evaporation of the juice.—After being clarified by one or other of the methods that have been examined above, the juice is concentrated to the state of syrup in the multiple-effect evaporator; one of the most important conditions for the efficient performance of this operation is naturally that no serious loss of sucrose shall occur. It is known that some destruction of sucrose can take place as the result of the temperature prevailing during evaporation; but experiments carried out by H. Claassen[25] have established that the amount due to this cause in the case of a triple-effect (in combination with a juice-heater) must be very small, probably only about 0·07% of the sucrose entering the factory. There is, however, another loss of sucrose, termed "entrainment," to which a good deal of attention has always been devoted. During the process of boiling *in vacuo* under the conditions usually obtaining in the sugar factory, a greater or less amount of this juice may be carried forward by the vapour in the form of a fine spray, for the retention of which a juice-separator or " catch-all " of some type or other is placed in the dome or in the steam line of the multiple-effect. It is generally considered that when using well designed apparatus, and when operating under certain conditions in respect of height of juice and degree of vacuum, little of the spray carried over by this priming effect escapes the separator to become lost in the water used for the condensation of the vapour. In fact, H. Pellet[26] found the loss by entrainment in French beet factories to be less than 0·14% when operating under the best conditions.

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[20] G.P. 322,135; *J.*, 1920, 668A.

[21] U.S.P. 1,326,159; *J.*, 1920, 201A.

[22] U.S.P. 1,327,222; *J.*, 1920, 275A.

[23] E.P. 134,607; *J.*, 1920, 37A.

[24] G.P. 320,846.

[25] "Verlustbestimmung." P. Herrmann. Page 155 *et seq.*

In a certain factory in Java, A. Schweizer[27] observed that after computing the sucrose left in the bagasse (exhausted cane), the filter-press cake, and the molasses, there was an unusually high loss arising from some unascertained cause, which from the weight and sucrose content of the juice before and after entering the multiple-effect he concluded could only have occurred during evaporation. Yet examination of the condenser water by means of α-naphthol and Fehling's solution (after concentrating the liquid) failed to reveal any appreciable loss due to spray passing the Hodek juice-separator. J. E. Abelous and J. Aloy[28] a short time previously had described experiments on the inversion of sucrose by the mechanical ionisation of water, in which they demonstrated that if 100 c.c. of a 5% solution of sucrose were passed five times through a Richardson vaporiser or " atomiser," about 0·06 g. of invert sugar is formed. Bearing this result in mind, Schweizer advanced the theory that the sucrose in the juice carried over during boiling may be " atomised " as the result of the very high speed of the steam in passing along the vapour line, and that while in this state decomposition occurs, not only to the stage of inversion, but even to the complete degradation of the molecule with the formation of carbon dioxide and water. J. G. van Ham[29] stated that he also was convinced of the high loss of sucrose in some factories in Java during concentration of the juice to syrup; that with the steam rushing through the vapour pipe and its elbows at the rate of about 100 ft. per sec. it was conceivable that the spray might be " atomised "; and that he considered the explanation advanced to account for the loss a likely one. F. G. E. Olsen[30] also concurred, and offered experimental evidence in support of the theory. He withdrew steam through two small pipes inserted in the main vapour line, one before and the other after the Hodek juice-separator, and found a comparatively considerable amount of sucrose accompanied by a little reducing sugars at the first point, but less sucrose and a much higher proportion of reducing sugars at the second. At the same time, he made continuous tests of the condenser water, but without finding any trace of sucrose. These results were cited as evidence that the entrained sugar was first inverted, and later totally destroyed, before it could reach the condenser.

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[26] *Bull. Assoc. Chim. Sucr.*, 1895–96, 342.

[27] *Archief Suikerind. Nederl.-Indië*, 1919, **27**, 2010; *J.*, 1921, 55A.

[28] *Comptes rend.*, 1919, **168**, 1125; *J.*, 1919, 475A.

[29] *Archief Suikerind. Nederl.-Indië*, 1919, **27**, 2098.

[30] *Ibid.*, 1919, **27**, 2161; *J.*, 1921, 55A.

Such a theory as this to account for the unknown loss of sugar during manufacture is not likely, however, to be accepted by many without much more definite experimental evidence; and an investigation of the question made later by J. S. de Haan[31] has yielded results leading to a much more reasonable conclusion. Generally in testing for the presence of sucrose in the waste water passing through a Torricellian condenser (the type largely used in factories in Java) a continuous sample is taken from the bottom of the fall-pipe; but the important observation was made by de Haan that the dense syrup spray does not become properly mixed with the water even by the time that it reaches the hot-well, a point that was submitted to proof in the laboratory by the use of a model apparatus. In fact in the case of a syrup at the comparatively high density of 85° Brix, the drops were found to reach the bottom of the column of water almost unchanged, and it was concluded that the only reliable procedure for the detection of loss by entrainment is to take a sample of the steam from the vapour line between juice-separator and condenser, though quantitative results can hardly be thus expected. On applying this method in certain factories in Java, in which the unknown loss of sucrose was unusually high, a considerable amount of entrainment was found to occur in all, the juice-separators in use (which generally were of the Hodek type) proving quite inefficient. When, however, an improved apparatus (utilising centrifugal force for the separation of the spray) was installed, and when, moreover, the level of the liquid in the several compartments of the multiple-effect was always kept below a certain height, results were obtained showing that the loss due to entrainment had been diminished to a negligible amount. Whereas formerly in one of the factories the unknown loss had been as high as 3·12%, it has now been reduced to 0·78%, a figure which when compared with the average value for all the factories in Java last year, viz., 2·59%, must be regarded as highly satisfactory.

De Haan's results are of much interest, and are certain at once to lead chemists to examine his important conclusion regarding the difficulty of detecting the presence of sugar in the condenser water, owing to the immiscibility of the drops of liquor carried over as spray. They will probably also again raise the question of the efficiency of different types of juice-separators, although after perusing these papers on the subject one is rather inclined to conclude that forcing the work of the evaporator beyond its normal capacity may have helped to induce the high loss by entrainment. It is an elementary principle that the juice during boiling must not exceed a certain height, the best separator being, as H. Claassen well remarks,[32] a lofty evaporating chamber. This is indeed the most important fact to be borne in mind in considering the question of entrainment: the chemist should determine the maximum height at which the man-in-charge of the evaporator may operate without danger of entrainment under the particular conditions prevailing in the factory, and he should also instal gauge-glasses on each of the compartments of the multiple-effect in order clearly to indicate this level.

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[31] *Ibid.*, 1920, **28**, 223; *J.*, 1921, 55A.

Quite another matter connected with evaporation concerns the establishment of the optimum limit to which the concentration of the juice should be carried in the multiple-effect before it is passed to the vacuum pans, where a better control of the conditions leading to the gradual formation of grain can be secured. In a symposium on this point, to which factory superintendents in Hawaii contributed, a rather considerable diversity of opinion was exhibited. R. J. Richmond[33] stated that he preferred working to 60°–65° Brix, or even lower when there is sufficient steam available; while H. Johnson[34] also gave 65° Brix as his figure, adding that when syrup of a higher density is taken into the pan the operators are apt to use too much water in endeavouring to form regular crystals. Most of those taking part in the discussion, however, expressed an opinion in agreement with J. P. Foster,[35] who asserted that the optimum should be regarded as being slightly lower than the point at which microscopic crystals appear when the syrup cools in the vacuum pan supply tanks, that is, 70°–75° Brix. H. D. Beveridge,[36] in concurring with this view, pointed out that when the factory is using fuel other than its bagasse, 1° Brix means a large saving of steam in the pans. He considered that with due care a sugar of good grain can be boiled from syrup of 70° Brix, or over, without the addition of any water, both time and steam being thereby saved; and the opinion of this contributor probably very fairly summarises the general attitude of technologists on the point.

Boiling to grain.—In the vacuum pan the syrup (or the molasses from a previous crop of crystals, or again a mixture of syrup and molasses) is boiled until it reaches the state of supersaturation, in order that the formation of crystals may occur. Crystallisation from an impure solution of sucrose is undoubtedly a complicated process, and among the factors which are known to control it are: time, degree of supersaturation; temperature, intensity of movement, number of grains under formation, and (not least) the quantity and nature of the impurities present in the syrup.

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[32] "Die Zucker-fabrikation." Fourth edition. Page 173.

[33] *Intern. Sugar J.*, 1920, 41-42.

[34] *Ibid.*

[35] *Ibid.*

[36] *Ibid.*

That there are yet other factors which may affect this phenomenon to a greater or less extent appears to be shown by the results obtained by P. J. H. van Ginneken.[37] Among these, attention may be drawn to the observation that if the solution be previously heated, the degree to which it is raised influences the rate of crystallisation. For example, some liquors were heated to 130° C., and others of identical composition and concentration to 110° C., when it was found after cooling all to the same temperature that the time elapsing before the formation of grain was greater in the case of the liquids that had been raised to the higher temperature, although no decomposition apparently had occurred. It was also found that if sucrose were repeatedly crystallised from aqueous solution, and re-dissolved, the time taken for the appearance of the first crystal became longer after each operation, the conditions of supersaturation, temperature, intensity of movement, and of composition, always being the same. Moreover, the time required for the re-solution of the crystals likewise successively increased. Other experiments demonstrated that apparently the history of the sugar is of some importance in regard to its crystallising properties. Thus, it was found that a pure sugar obtained by precipitating a concentrated aqueous solution of refined sugar with alcohol, and washing with alcohol and ether, crystallises more slowly than the refined sugar from which it was prepared (the small amount of impurities present in the original sample being proved to be without any influence). H. C. Prinsen Geerligs[38] states that he is able to confirm certain of these results; while it may also be recalled that T. van der Linden[39] in one of his recent papers directed attention to the circumstance that a certain cane molasses, which on cooling readily gave a crop of small crystals, failed to do so when the grain was re-dissolved and the liquor cooled under apparently the same conditions as previously. These observations obsure rather than elucidate our understanding of the phenomenon of grain formation in sugar manufacture, which is certainly a subject of which our knowledge is still inadequate. It is therefore to be hoped that the experiments begun by van Ginneken may be continued for the purpose of furnishing further information, which ultimately may lead to a greater dependence on scientific methods in sugar boiling than obtains at the present time.

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[37] *Chem. Weekblad*, 1919, **16**, 1210; *J.*, 1919, 784A.

[38] *Intern. Sugar J.*, 1920, 469.

[39] *Archief Suikerind. Nederl.-Indië*, 1919, **27**, 1517.

It was pointed out last year that in concentrating the syrup to grain to obtain the mixture of crystals and molasses known as massecuite, it is no longer general practice to proceed according to the method of repeated boilings, by which first, second, and third crops of crystals are successively obtained from the syrup, the first molasses, and the second molasses. Systems of "boiling in" the molasses, which are more economical in respect of labour, time, and floor-space, are now used; and a procedure followed in Cuba with good results was described.[40] It is now worth while noticing the relative merits of two boiling processes which have been tried by G. E. G. von Stietz[41] in a certain factory in Java.

In the first process, four successive boilings or "strikes" were made, these being: (1) using syrup of 85°–90° purity from the evaporator with some returned molasses sugar, the Brix being 91°–93° and the purity 85°–90°; (2) using evaporator syrup, some molasses from the first strike, and some returned molasses sugar, the Brix being 93°–94°, and the purity 80°; (3) using evaporator syrup and molasses from the second strike, the Brix now being 94°–95°, and the purity 70°; and (4) using evaporator syrup and molasses from the third strike, the Brix being 98°–99° and the purity 60°, a waste molasses of about 32° purity (apparent) being obtained. These three crops of crystals were mixed together, giving a raw sugar having an average polarisation of 98°–99° and a colour of 16°–20° Dutch standard; while (as mentioned) the fourth crop was returned to build up the first and second strikes. When operating this method, however, some difficulty was experienced, owing to the unexhausted molasses remaining too long in circulation, the "curing" (or separation of the molasses in the centrifugal machines) also being often faulty. Further, the black fourth sugar by being returned to the first and second strikes re-introduced a certain amount of very viscous molasses, and it was found after a time that the polarisation of the mixed raw sugar fell short of 98°. In the early part of the season matters went well enough; but latterly as the circulating molasses became more and more "gummy," the work became more and more troublesome, a result that indeed might be anticipated, especially if the purity of the syrup coming from the evaporators were rather low.

Therefore the scheme here illustrated was followed, in which exhaustion to the stage of final molasses was more rapid and more direct :—

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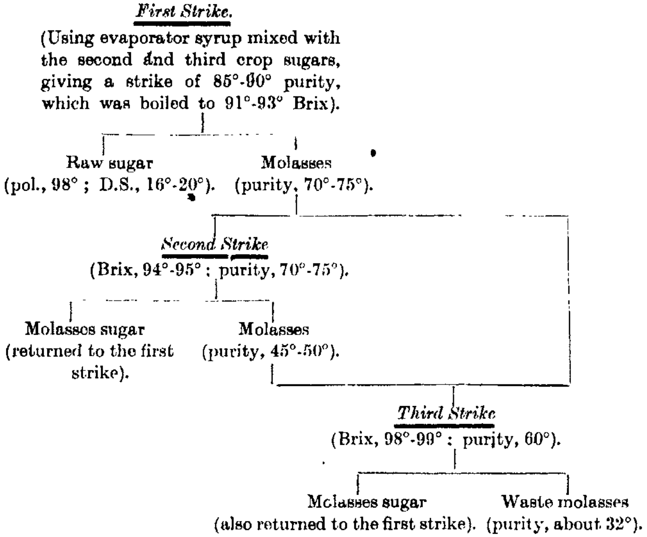
[40] *Ann. Repts.*, 1919, **4**, 382.

[41] *La. Planter*, 1920, **65**, 92; *J.*, 1921, 22A.


First Strike.
(Using evaporator syrup mixed with the second and third crop sugars, giving a strike of 85°-90° purity, which was boiled to 91°-93° Brix).
Raw sugar (pol., 98° ; D.S., 16°-20°).
Molasses (purity, 70°-75°).
Second Strike
(Brix, 94°-95° ; purity, 70°-75°).
Molasses sugar (returned to the first strike).
Molasses (purity, 45°-50°).
Third Strike
(Brix, 98°-99° ; purity, 60°).
Molasses sugar (also returned to the first strike).
Waste molasses (purity, about 32°).

Boiling the first strike was found to be particularly easy, since it was not required to granulate, but only to evaporate the mixture of syrup and molasses to cause the growth of the crystals already present ; to take in more syrup until the pan was full ; and finally to drop the massecuite down to the crystallisers, where, while gradually cooling, further growth on the existing grain could proceed. As is shown, the second strike was boiled with first molasses alone, and the third with first and second molasses, lastly obtaining an "exhausted" molasses of 30°–32° purity (apparent). It will be observed that in the first boiling all the evaporator syrup is used, together with all the second and third crop sugars, thus making this strike the largest of all. Compared with the method previously in use which has just been described, improved results would be anticipated from this system of boiling, its great advantage being that all the merchantable sugar is obtained in the first boiling, so that a product of good and even quality should be expected.

Centrifuging and finishing.—It now remains to separate by means of the centrifugal machine the mixture of crystals and molasses composing the massecuite, and in so doing the main conditions for success are (A) that the crystals should be well formed and of fair size ; (B) that "false grain" should be absent ; and (C) that the molasses should not be too viscous.

Difficulty continues to be experienced in Hawaii in curing the massecuite for the production of 96° polarisation sugar for the American refineries; and W. McAllep[42] points out that the principal cause of this in connexion with the second strike is the presence of "false grain" (very fine crystals, which have inadvertently been allowed to appear subsequently to the grain proper,[43] and that for its avoidance slow boiling is most important. An even grain should be first formed in the pan, and the massecuite concentrated carefully to a high density, taking as long as 12 hours to do so, the purity of the mother-liquor being reduced as low as possible before dropping to the crystallisers. He considers it desirable that the crystals should be about 3 mm. in diameter; and he has observed that when the grain is larger, and when the massecuite is concentrated to a high density, false grain forms, either in the pan, or in the crystallisers, or in both.

In regard to the third condition for securing the best separation of crystal and mother-liquor, R. C. Pitcairn[44] states that after trying a number of methods of treating the massecuite for the purpose of lowering its viscosity, he has obtained good results by allowing it to flow over a number of inclined shelves placed one above another in a box through which dry steam was passed. This procedure is suggested as a simple means of conveniently and economically heating the massecuite to about 35° C., the effect of which slight rise of temperature was to reduce the time ordinarily necessary in centrifuging by 25–35%, though whether at the same time the purity of the molasses is increased by the solution of some of the crystal (as would appear likely) is not mentioned. At any rate, it would seem certain that the water content of the massecuite, as the result of the condensation of steam, must be increased to some extent. W. Lougher[45] practises the addition of diluted waste molasses to the massecuite just previous to centrifuging, believing this to be a convenient and harmless method of decreasing the viscosity; while H. S. Walker[46] prefers to add hot waste molasses to the massecuite in the centrifugal immediately after the machine has been started.

It is worth calling attention to the fact that several factories in Hawaii are now cooling and drying their sugar by passing it through a Hersey apparatus previous to sending it to the packing department.[47] This practice is very commendable. It prevents "caking" in the bags during storage; it eliminates largely the difference in weight observed at the colonial factory and the home refinery; and lastly (and by no means least) it decreases the risk of deterioration during transit by lowering the "factor of safety," a matter that has recently been very fully investigated by C. A. Browne[48] and W. L. Owen.[49]

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[42] *Intern. Sugar J.*, 1920, 208.

[43] *Ann. Repts.*, 1919, **4**, 383, 395.

[44] *Intern. Sugar J.*, 1920, 525.

[45] *Ibid.*, 1920, 208.

[46] *Ibid.*, 1920, 160.

[47] *Ibid.*, 1920, 42, 161.

The Beet Sugar Industry.

British beet sugar.—There is no development of note to record in regard to beet sugar projects in this country. Kelham factory is in course of erection, and is expected to commence slicing roots in the autumn of 1921. Cantley factory has been bought by a syndicate formed by a Liverpool firm of sugar merchants, and it is stated that it will be used, not only as a raw beet factory, but (between seasons) as a refinery for dealing with raw cane or beet sugars.

Extraction of the juice.—In the early days of beet sugar manufacture the juice was extracted by rasping and pressing; but at the present time the method almost exclusively employed consists of the systematic lixiviation of the sliced roots in a battery of cylindrical vessels termed "diffusers," in which at a suitable temperature the crystalloidal constituents, *e.g.*, sugars and salts, and other molecular dispersoids, are caused to dialyse through the walls of the plant-cells into the water or weak juice surrounding them, while the colloidal impurities, *e.g.*, proteins, pectins, and gums, for the greater part remain behind. Other methods of extraction have been proposed from time to time, and the best known of these is the Steffen scalding process, in which the beet slices after being mashed in hot juice are simply pressed, hydraulically or otherwise. In this way about 70–75% of the sugar is obtained in the form of juice, and the rest remains in the residue of pulp, which is sold as a saccharine cattle food. Obviously the principal advantage of such a process, compared with ordinary diffusion, is its simplicity; while its great objection is the low yield of marketable sugar that may subsequently be obtained. It is of some interest, however, to note that in Germany during the war a process of extraction on somewhat similar lines was developed, by means of which it appears possible to realise a much higher yield than in the "sugar fodder process"—as high in fact as in battery diffusion. Not the least of its several advantages is that the accumulation of waste water resulting from the pressing of the exhausted pulp (the disposal of which is a problem still engaging attention[50]) is entirely suppressed.

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[48] *Ann. Repts.*, 1918, **3**, 370.

[49] *Ibid.*, 1919, **4**, 385.

[50] *Z. Ver. deuts. Zuckerind.*, 1920, 163; *J.*, 1920, 420A.

The evolution of this so-called "rapid" extraction method may be briefly traced. It is based upon H. Bosse's scalding process,[51] according to which the slices on leaving the cutting machine are made to fall through a space filled with steam at 103° C. with the object of raising them to about 90° C., an advantageous temperature with which to commence diffusion in the battery. It was observed when this process was put into operation that the slices absorbed the steam with great avidity, and later experiments demonstrated that about 80% of the sugar could be extracted from the slices thus treated merely by once pressing them in a Klusemann, Bergreen, or other suitable apparatus now in use for exhausted pulp. As a matter of fact, during the war when fodder was scarce this simple method proved of considerable service, as S. Thieler[52] points out, giving good results even with frozen roots, the treatment of which in the battery is difficult, and sometimes impossible. Attempts were made to increase the yield of sugar in the juice by mashing the partly exhausted pulp with hot water, and again pressing; but improved results were only obtained when the slices after being steamed were passed along a trough while being sprayed with water or weak juice, the diffusion of the sugar through the walls of the plant-cells that had remained unruptured being thus given an opportunity to occur. At first a trough in which slices and juice were both moved along in the same direction from one end to the other by means of revolving arms was used; but the successful operation of the method as now evolved is due to the invention of a special trough, along which it is possible to move slices and juice in counter-current without the goods being subjected to any considerable pressure at any stage of its progress.

This "rapid" trough has been patented by M. Paschen,[53] and its method of use has been further described by S. Thieler.[54] One of the latest types has a length of about 22½ m., and a diameter of 1·7 m., and is divided into 20 compartments. It is placed at an angle of 4° to the horizontal. By means of suitable arms attached to a slowly revolving shaft running the whole length of the apparatus, the slices are conveyed from the bottom to the top end of the trough, through each compartment, and over each dividing wall; while the water enters the top end, thus flowing in counter-current to the slices from compartment to compartment through perforations in the dividing walls, lastly leaving the lower end of the apparatus in the form of juice. During the 1915-16 season, a "rapid" plant having the general construction shown in the illustration was in operation in the Bük (Hungary) factory, in which at the same time ordinary battery diffusion was employed.

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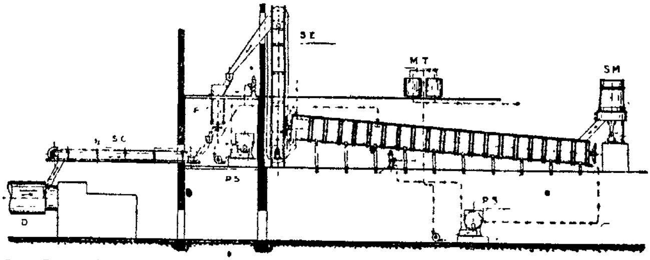
[51] G.P. 244,260; U.S.P. 1,005,931; *J.*, 1911, 1326.

[52] *Zentr. Zuckerind.*, 1920, **28**, 468; *J.*, 1920, 828A.

[53] G.P. 278,067; U.S.P. 1,134,152; *J.*, 1915, 567A.

[54] *Zentr. Zuckerind.*, 1920, **28**, 492; *J.*, 1920, 828A.



On dropping from the slicing machine (SM), the slices were met by steam at 108°–110° C., which raised them to 85°–90° C., at which temperature they entered the first compartment to commence their journey to the top of the trough, fresh water at 55°–60° C. being allowed to flow into the twentieth. When the slices arrived at the top, they were raised by an elevator (SE) and dropped while still hot into the pulp-presses (P), the resulting residue being sent by means of the conveyor (SC) to the pulp drier (D), while the expressed juice was returned *via* a pulp separator (PS) to the trough at its fifteenth compartment. The juice leaving the lower end of the trough had a temperature of 75°–85° C., and after going through a pulp separator (PS) it was pumped to the measuring tanks (MT), lastly being passed to the clarifying department. Altogether the slices remained 25 min. in the trough, the capacity of which was about 240 tons in 24 hours.

Coming now to the results obtained, the sugar content of the slices was found to be about 0·4% (of the roots) in the new method, the total amount of juice drawn off being about 130% (also of the roots); while in ordinary battery diffusion with a draw-off of about 140%, the amount of sugar left in the slices when added to that lost in the waste waters amounted practically to the same figure. A rather important point to note in respect of the juice drawn off is that, compared with battery diffusion practice, its density was about 3° Brix lower, which difference, H. Claassen[55] points out, would mean about 1% more coal to supply the additional steam required for the elimination of the greater amount of water. On the other hand, S. Thieler[56] contends that this increased cost is quite compensated by economy of labour (two men fewer per shift); by the saving of steam for heating the juice previous to clarification; and lastly by decreased repairs. Other independent trials with this new process of extraction are necessary before a trustworthy decision upon its value can be pronounced; but the particulars published so far certainly impress one as to its practicability. That the formation of waste water is suppressed, and that the extraction of sugar is no less than in ordinary diffusion, are both very favourable points. In regard to the weaker juice produced, it yet remains to be seen whether it would not be possible to obtain an increased density by lengthening the trough, say, to 25 or 30 compartments, the draw-off remaining the same. In this way it might prove possible to produce a juice having a density greater than that ordinarily obtained by battery diffusion, and it will be of interest to observe the result of any experiments that may be made in this direction.

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[55] *Zentr. Zuckerind.*, 1920, **28**, 565.

[56] *Ibid.*, 1920, **28**, 522.

Clarification of the juice.—Beet juice as it comes from the diffusion battery is a turbid, dark-grey or almost black liquid, which cannot be filtered in factory practice, owing to the "slimy substances" it contains. At the present time its clarification is universally effected by the carbonatation process, in which, after passing through suitable strainers for the elimination of fine pulp, it is heated to 80°–85° C.; treated with caustic lime (either in small lumps or already slaked in the form of milk, using 2½–3% CaO of the roots sliced); "saturated" with carbon dioxide to an alkalinity of 0·09–0·13% CaO; filtered; re-heated; again carbonated, this time to 0·02–0·04%; and finally again heated and passed through filter-presses.

A considerable amount of work has been done in establishing the effect of the treatment with lime upon the impurities of the raw juice, especially the acids, proteins, pectic bodies, invert sugar, and colouring matters; but little attention appears to have been given to what is generally designated in the literature of beet sugar manufacture as the "mechanical action" of the precipitate resulting on the addition of lime, and particularly of that formed later on carbonating. This so-called "mechanical action" is, indeed, hardly less important in realising the proper clarification of the liquid than is the chemical action of the lime on the non-sugar substances. Thirty years ago K. C. Neumann[57] pointed out distinctly that the clarifying operation in beet sugar manufacture must be regarded as something more than the mere formation of calcium carbonate, and that the "spongy" nature of the precipitate accounts for the absorption, not only of the suspended matter, but also to a greater or less extent of the colouring substances and other soluble impurities present in the juice, experience having shown that the greater its volume the more completely are these results achieved. In view of observations such as this, it really seems surprising that Continental investigators have not more definitely described this "mechanical action" of carbonatation as a colloidal phenomenon, a point of view which (as we have seen on page 22) has now been adopted in regard to the clarification of juice in the sister industry.

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[57] *Z. Zuckerind. Böhm.*, 1890–1, **15**, 369.

Certain modifications of the carbonatation process which have recently been proposed show the advantages of this conception in regard to carbonatation. Actually the amount of lime required to cause the chemical changes capable of occurring is only about 0·2% ; but experience very clearly shows that if much less than 2½–3% (and sometimes 3½ and perhaps even 4% in the case of inferior roots) be used, filtration becomes difficult and sometimes impossible. As one would expect, attempts have been made to reduce the amount of lime stated, in order thus to cheapen clarification. Thus, E. Kuthe and E. Anders[58] about 31 years ago protected a method of operation in which only the amount of lime necessary for chemically reacting upon the impurities was applied, some calcium carbonate obtained from the previous treatment of the juice being added to supplement the smaller amount formed on subsequently passing in the carbon dioxide ; but careful trials made with this process in a number of factories under different conditions failed to prove that any appreciable economy in lime could thus be effected. Another method of working, devised by K. Kowalski and S. Kozakowski,[59] consisted in the addition of lime to effect complete precipitation (A) in the cold, and (B) on heating, the amount of lime to be added at each stage being determined by means of preliminary laboratory tests, in which a slight excess was added and the liquid titrated back with tannic acid. Nor is this modification used any longer. It would appear that the failure of both processes is due to the fact that there is a certain minimum quantity of calcium carbonate which must be formed in the body of the juice to effect the sufficient adsorption, not only of the coarser dispersoid, but also of the colloidally dispersed impurities (particularly pectic substances and colouring matters). Many years' experience now appears to have proved conclusively that if less be precipitated than this amount (which will vary to some extent according to the purity of the juice treated), an insufficiently clarified liquid will certainly result.

Notwithstanding the teaching of practice in this direction, another modification of the carbonatation process, which may be regarded as a combination of the Kuthe and Anders and the Kowalski and Kozalowski procedures, has been elaborated by E. Psenicka [60] It consists in mixing the cold diffusion juice with 10–20% of its weight of the unfiltered clarified juice (containing the precipitated calcium carbonate) together with 0·2–0·4% of lime, after which the liquid is heated to 90°–95° C., treated with 1·0–1·5%

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[58] G.P. 50,032.

[59] G.P. 138,693.

[60] G.P. 318,654 ; *J.*, 1919, 592A ; 1920, 421A.

of lime, carbonated to an alkalinity of 0·08–0·10% CaO, and filtered, the clear juice being lastly submitted to a second saturation, in order further to reduce its alkalinity. This method of working has been examined by V. Stanek,[61] in comparison with ordinary carbonatation, using the same amount of lime in both cases, namely 2%, but the results obtained must be regarded as being only slightly in favour of the proposed procedure. Thus, the coefficient of purity of the juice was 94·95° and 94·60° respectively, its colour 1·5° and 1·81° Stammer, and its content in lime salts 0·0031 and 0·0041% CaO, differences which are quite small, and might very well occur as the result of slight variations in the ordinary operation of carbonatation. It would therefore seem that more decisive results are required in order to convince manufacturers that this modification is more advantageous than the Kuthe and Anders method, which indeed it much resembles.

Another deviation from the ordinary routine of the carbonatation process, which appears to have a bearing on the subject of the adsorbing power of the precipitate produced during that operation, may be briefly noticed. H. Claassen[62] proposes preliminarily to treat the juice with just sufficient lime to throw out of solution as much non-sugar as possible without the formation of insoluble calcium compounds, the precipitate thus obtained being separated and the filtrate subsequently limed and carbonated as usual. This modification has as its purpose the separation of a precipitate rich in albumin and low in mineral matter which might serve as a cattle food ingredient; and M. von Wierusz-Kowalski[63] has protected a somewhat similar method of working. These two procedures appear to have been suggested in Germany during the war, at a time when sources of cattle food were being eagerly sought there; but an examination of their value made by the Institut für Zuckerindustrie[64] shows the product of both to be too high in mineral matter to be regarded as useful additions to fodder. Apart from this, however, such modifications of the ordinary method of carbonatation appear undesirable from the point of view of attaining the maximum clarification of the juice possible. It is pointed out by A. Herzfeld[65] that precipitates preliminarily separated in this way contain in addition to albumin some very fine pulp, with which in the ordinary course of operating the excess of lime forms a precipitate possessing a considerable clarifying power, or, in other words, a high power of adsorption towards the colloidal impurities present in the raw juice, acting, it would seem, very much in the same way as the bullock's blood of the old-time refiner. He based this statement on the fact that the juice obtained in the Steffen process of extraction (which contains an unusually high amount of fine pulp) yields after carbonatation, a clarified liquid both purer and lighter in colour than does diffusion juice submitted to similar treatment. Observations such as these, if interpreted in the light of the colloidal nature of clarification, are of much interest, and later may prove to be of considerable value. It is hoped that in the near future investigations will be undertaken for the purpose of examining the "mechanical action" taking place during liming and clarification; of establishing more exactly its importance; and also of ascertaining the optimum conditions for its operation.

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[61] *Z. Zuckerind. Czechoslov.*, 1919, **44**, 73.

[62] G.P. 307,575; *J.*, 1919, 26A.

[63] G.P. 306,410.

[64] *Deut. Zuckerind.*, 1920, **45**, 244.

[65] *Ibid.*, 1920, **45**, 243.

Boiling to grain and finishing.—In regard to the remaining stages of beet sugar manufacture, viz., crystallising, centrifuging, finishing, and working up the after-products, unfortunately the work published during the last year has been scanty and disconnected, and hardly calls for comment here. It remains only to draw attention to a process protected by P. Kestner [66] for the elimination of the obnoxious flavour and odour of beet syrup, consisting simply in raising the temperature during evaporation to a rather high degree for a short time. He proposes to utilise it for the production of what he terms *sucre complet* (or "whole juice sugar") by boiling the entire syrup to a mass without separating the crystals from the mother-liquor, as is the general practice except in the manufacture of crude grades by native methods. Clarification would be effected only by the addition of a little lime to the diffusion juice, after which it would be filtered at a high temperature through presses, and concentrated to about 60° Brix (preferably in a film evaporator), the syrup obtained being crystallised while stirring, so that a very fine-grained product would result. Thus, carbonatation, centrifuging, and the recovery of the low products from the molasses are avoided; and it is urged that such a method of working should be found advantageous at the present time in France, in order to aid in supplementing the much diminished supply, small factories containing the necessary plant (mainly diffusers, filter-presses, evaporators, and "finishers") being erected at convenient centres in beet growing areas. It is claimed that the crude greyish-yellow sugar thus obtained is of good taste, and that it can be exposed for a reasonable time to a humid atmosphere without any apparent alteration of condition, although hygroscopic to some extent, owing to the presence of potassium salts. It is said to meet many of the requirements of the chocolate, biscuit, and confectionery industries; to be suitable for the sweetening of coffee; and also to be capable of forming palatable and nourishing products when mixed with cocoa and condensed milk.[67]

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[66] E.P. 135,235; *J.*, 1920, 76A.

[67] E.P. 136,205; *J.*, 1920, 170A.

This method of manufacturing a crude sugar (though certainly retrograde in character) may prove of some temporary use for the relief of the situation in France, and for this reason its adoption is supported by L. Lindet,[68] J. Weisberg,[69] and others. Its value will, of course, almost entirely depend upon the extent to which it is successful in producing a sugar free from the disagreeable "beety" flavour, a point which should be proved during the trials that are now being made at the Pithiviers factory (Loiret), France. In times when the sugar supply is normal, a simple method of destroying or transforming the substances contributing to the obnoxious taste and odour (a problem that has been attacked by several different experimenters[70]) would be of value for the preparation in beet factories of a quality of syrup suitable for use on the table or in the fruit-preserving industry. An efficient process would probably establish beet syrup as an important article of food on the Continent. It may be noted that an effort to do this has already been made in Germany, where table syrup of fair quality (though hardly as palatable as the product to which we are accustomed in this country) is being prepared directly from the beet, a method of working patented by W. Meyer[71] being used in several factories.

Analysis of Sugar Products and the Results of Chemical Control.

Determination of sucrose.—Much attention has been devoted during recent years to the Clerget or double polarisation method of determining sucrose with the object of yet further increasing its accuracy, so as to provide a means both precise and convenient of obtaining the most reliable estimate possible of the sources of loss of sugar at the different stages of manufacture. An important advance in this direction has been made by an investigation carried out by the Bureau of Standards, Washington; but before considering this contribution it seems worth while briefly tracing the history of the double polarisation procedure as generally operated at the present time in sugar factories.

Actually it was Biot[72] who first proposed to determine sucrose by observing its rotation before and after inversion; but the polarimeter of his day was in its earliest stage of development (an adjustable mirror of black glass serving for the polariser), and the method he described so lacked detail that it could hardly be considered a quantitative one. Clerget's original process[73] was published a few years after the invention of the Mitscherlich instrument; and for the direct reading he used the liquid obtained by dissolving the normal weight of the sample (then 16·471 g.) in water, adding basic lead acetate solution, completing the volume to 100 c.c., and filtering; while the inversion polarisation was made by placing 50 c.c. of the filtered clarified solution in a flask graduated at 50 and 55 c.c., adding 5 c.c. of concentrated hydrochloric acid, mixing, and slowly heating the flask in a water-bath to 68° C., taking about 10 minutes in so doing, lastly cooling and filtering. Operating in this way, he found that while a solution of pure sucrose before inversion gave a reading of $+100·0$, it gave after inversion a value of $-44·0$ at 0° C. (corresponding to $-34·0$ at 20° C.); and the formula based on these results which he gave for the calculation of the sucrose per cent. was:

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[68] *C. r. Acad. Agric.*, 1920, **6**, 291.

[69] *J. Fabr. Sucre*, 1920, **61**, No. 7.

[70] E.P. 133,744; U.S.P. 1,155,806; *J.*, 1919, 960A.

[62] G 319,841; *J.*, 1920, 669A. *Cf.* also "Rübensirup, seine Herstel-

[63] G.P. 306,410. 1920. (Otto Spamer, Leipzig.)

[64] *Deut. Zuckerind.*, 1920,

[65] *Ibid.*, 1920, **45**, 243.

$$\frac{100(D-I)}{144·0-\frac{1}{2}t}$$

in which D and I are the direct and inversion readings, and t the temperature at which the inverted solution is observed in the polarimeter tube. When applying this method to the examination of impure products, *e.g.*, final molasses, it was found that the solution obtained after inversion was so dark that the observation of its polarisation in the 200 mm. tube was often impossible without dilution (and consequent diminution of the accuracy). Principally with the object of overcoming this difficulty, Reichardt and Bittmann[74] modified the procedure, employing in so doing the normal weight that had been adopted in Germany They used for the direct reading a solution clarified with basic lead acetate, as Clerget had done; but the inverted solution was prepared by dissolving 13·024 g. (half the normal weight) in 50 c.c. of water in a 100 c.c. flask, inverting with 5 c.c. of concentrated hydrochloric acid by heating to 67°–70° C. for 15 minutes, cooling, and making up to the mark, this liquid being decolorised by the addition of powdered animal charcoal and filtered. These German investigators, however, still used Clerget's factor of 134 at 20° C. for the calculation of the result, it being unknown at that time that the specific rotation of invert sugar under the conditions of this determination depends upon its concentration, and also upon the amount of hydrochloric acid present, observations that were made later by Gubbe.[75] Subsequently Creydt[76] gave 132·4 at 20° C. as the appropriate factor to use for a concentration of 13·024 g. of sucrose in 100 c.c., when inverted under the conditions of the Reichardt and Bittmann procedure. Until that time, workers had failed to take account of a serious error, namely, that arising from the rather ready destruction of the lævulose of the invert sugar by the hydrochloric acid used for hydrolysis. Wohl and Dammüller[77] pointed out that 8 minutes sufficed to effect complete hydrolysis of the sucrose, and that by extending the time to the 15 minutes used by Creydt and others, the lævo-rotation of the reading was appreciably diminished.

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[74] *Z. Ver. Rübenzuckerind.*, 1882, 764.

[75] *Ibid.*, 1884, 1345.

[76] *Ibid.*, 1887, 153.

With the purpose of establishing the optimum conditions for avoiding the destruction of the lævulose, and of generally improving the double polarisation method, a careful series of experiments was made by A. Herzfeld and his assistants at the Institut für Zuckerindustrie, Berlin, in 1888.[78] They concluded that the concentration of the solution used for inversion should be 13·024 g. dissolved in 70 c.c. of water (contained in a 100 c.c. flask), instead of the 50 c.c. hitherto used, the slightly greater dilution diminishing the lævulose destruction perceptibly; that the amount of hydrochloric acid should be 5 c.c. of 38% concentration (sp. gr. 1·18); and that the total time of heating should be 7½ minutes, 2–3 minutes of this being taken to raise the temperature to 68°–70° C., after which the liquid should be maintained as near 69° C. as possible for exactly 5 minutes, cooled rapidly, made up to 100 c.c., and read in the 200 mm. water-jacketed tube after carefully observing the temperature. They also concluded that a total time of heating in the manner indicated sufficed to invert all the sucrose present even when examining products having a high ash content; while at the same time the error due to lævulose destruction was reduced to the minimum possible. Under the new conditions specified, the factor became 132·66 at 20° C. (instead of 132·4) for the concentration of 13g. in 100 c.c., and a table of factors corresponding to other concentrations was elaborated. This modification of the double polarisation method by Herzfeld and his collaborators has now come to be regarded by reason of its convenience as the standard procedure for the routine determination of sucrose in factory and refinery products. During the past few years, however, several workers have pointed out a source of error that cannot be ignored, namely, that the difference between the direct and inversion readings is not due wholly to hydrolysed sucrose, since certain optically-active impurities are capable of altering the rotation according to the reaction of the liquid. Thus, the observation of the direct reading taken in the presence of the basic lead acetate used for clarification is not comparable with that of the inverted liquid containing the hydrochloric acid used for effecting hydrolysis. V. Stanek[79] showed the interfering substances to be principally amino-acids in the case of beet products; while J. P.

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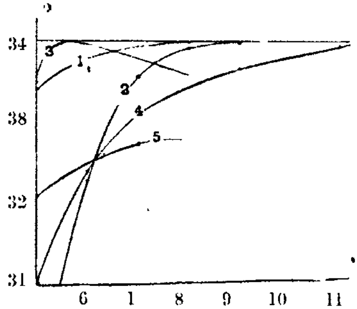
[77] *Ibid.*, 1888, 742, 763.

[78] *Ibid.*, 1888, 707.

[79] *Z. Zuckerind. Böhm.*, 1906–7, **31**, 417.

Ogilvie[80] in the case of cane products pointed out that the reducing sugars present, owing to the difference of their rotation in the presence of basic lead acetate and later of hydrochloric acid, are capable of vitiating the result to the extent of about 1·5%.

Coming now to the work carried out at the Bureau of Standards, Washington, by R. F. Jackson and C. L. Gillis,[81] results are given showing that when hydrolysis is effected at 68°–70° C., there occurs at the same time a comparatively rapid destruction of the invert sugar, this corresponding to a decrease of 0·056° (sugar scale) per minute. Curve 3 shows the rate of inversion under Herzfeld's conditions, the maximum lævo-rotation being reached in about 5 minutes, after which the polarisation falls rapidly on account of lævulose destruction. On the other hand, curves 1 and 2 indicate the course of inversion at the lower temperature of 60° C., at which degree (with the same sucrose concentration) the reaction is complete in 8½ minutes; and it is contended that "if the inversion is carried out under such conditions that the end of the reaction is situated on a broad and flat portion of the curve, relatively large differences in individual procedure can be tolerated without a diminution of accuracy. . . . Under these conditions, the accuracy of the Clerget divisor itself is limited only by the precision with which polariscopic observations can be made." This modification involving hydrolysis at 60° C. is therefore recommended, and it was found to result in a factor of 133·25 at 20° C. for a concentration of 13 g. per 100 c.c., in place of Herzfeld's 132·66. That during inversion at 60° C. no appreciable destruction of invert sugar occurs, and that therefore the proposed new procedure is preferable to the Herzfeld method, is proved by the circumstance that a factor of 132·00 was obtained when using invertase as the hydrolyst, which value in the presence of the hydrochloric acid used for the



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[80] *J.*, 1911, 62.

[81] *Sci. Paper No.* 375, *Bureau of Standards*, 126; *J.*, 1920, 634A.

ordinary acid hydrolysis (5 c.c. of 38% acid in 100 c.c.) became 133·24, thus corroborating the result obtained by acid hydrolysis at 60° C.

Not the least interesting part of the contribution by Jackson and Gillis is that which deals with the obviation of the error caused by the change of rotation of optically-active substances other than sucrose on the addition of the hydrochloric acid employed for inversion. This is accomplished in the case of beet products by neutralising the inverted liquid with ammonia solution, an amount of ammonium chloride equivalent to that thus formed being added to the liquid used for the direct reading, both observations being made in this way under comparable conditions. In the case of cane products, the alteration of the reducing sugars when the liquid is read in the presence of basic lead acetate, and later in that of hydrochloric acid, is overcome by the fortunate observation made by these investigators that sodium chloride affects the rotation of reducing sugars in the same direction as hydrochloric acid. If, therefore, a suitable quantity of sodium chloride be added to the liquid used for the direct polarisation, the effect upon the rotation of the lævulose of the 5 c.c. of hydrochloric acid employed for inversion can be duplicated, and comparable conditions of observation again secured. This research carried out at the Bureau of Standards is one of the most useful and complete published on the determination of sucrose during recent years. Although it remains to examine their conclusions more closely in the laboratory, and particularly to compare the results given by the new method with those obtained by the use of invertase (which acts as a selective hydrolyst without affecting non-sugar substances), it would seem that these American workers have succeeded where a number of other investigators have failed, namely, in obviating the error due to the presence of optically-active substances other than sucrose by means of a reasonably convenient and practical modification.

Determination of reducing sugars.—Fehling's solution is in almost general use in sugar factories and refineries for the determination of reducing sugars; but it is well recognised that this reagent possesses the marked disadvantage of attacking sucrose to an extent that is not inconsiderable (owing to the large amount of sodium hydroxide it contains), reducing sugars being formed for the presence of which an allowance must be made in the case of products containing a large proportion of the disaccharide. Soldaini[82] and other chemists have endeavoured to overcome this defect by using a solution of copper bicarbonate; but the reagent prepared according to their formulæ did not prove very satisfactory. Its effect upon sucrose was certainly less than that of Fehling's solution; but it did not keep well; it deposited cupric hydroxide; and it precipitated lime and other mineral impurities from the sugar product being examined. Ost,[83] however, was more successful in preparing a more generally stable and reliable cupric bicarbonate liquor, and this he did by adding a solution of copper sulphate to a solution containing both potassium carbonate and bicarbonate, instead of trying to dissolve copper carbonate in a solution of potassium bicarbonate, as others had done. Schmoeger[84] and Degener[85] published favourable reports upon this formula.

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[82] *Z. Ver. deuts. Zuckerind.* 1885, 625; 1888, 628.

As the result of a long examination of the question, P. Beyersdorfer[86] has now come to the conclusion that although Ost's solution cannot be regarded as an altogether ideal reagent, it is at any rate preferable, generally speaking, to Fehling's. Using 10 g. of refined sugar, and operating according to the Herzfeld gravimetric procedure, the cupric reduction was found to be only 3·8 mg. in the case of Ost's, and 30 in that of Fehling's solution. In regard to sensitiveness, it was found that 1 mg. of invert sugar in the presence of 10 g. of sucrose could be detected by Ost's solution; whereas less than 5 mg. under like experimental conditions could not be definitely found by means of Fehling's. It appears premature yet to pronounce upon the keeping quality of the cupric bicarbonate liquor, but it was observed that when exposed to sunlight in white glass flasks its titre remained unchanged for at least 2 months. This contribution of Beyersdorfer should induce sugar factory and refinery chemists to experiment in the same direction, and the publication of their experience with a reagent so well recommended in comparison with Fehling's solution should certainly be of value. Already, it may be noted, F. J. Bates[87] has used this cupric bicarbonate liquor for the determination of traces of reducing sugars in refined sugars, the detection of so small an amount as 0·003% being claimed.

Chemical control results.—Returns giving the result of the very careful chemical supervision exercised in Java are always interesting. It is noticeable in the tables for 1919[88] that the extraction (sucrose in the juice per cent. sucrose in the cane) still remains in the neighbourhood of 92%, a value that compares indifferently with the figure of 97–98% now averaged in Hawaii.[89] On the other hand, the remaining factory data show admirably efficient work, as, *e.g.*, the sucrose content of the filter-press cake of the clarification department, which is decreasing each year, and is now 3·7% (or

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[83] *Ibid.*, 1890, 361; 1891, 97.

[84] *Ibid.*, 1891, 785.

[85] *Deuts. Zuckerind.*, 1897, 71.

[86] *Z. Ver. deuts. Zuckerind.*, 1919, 403; *J.*, 1920, 126A.

[87] *Intern. Sugar J.*, 1920, 654.

[88] *Ibid.*, 1920, 322; *J.*, 1920, 579A.

[89] *Ann. Repts.*, 1919, **4**, 378.

0·06% on the cane), about half the figure for 1910. Other values that are satisfactory are the sucrose remaining in the bagasse, which was 0·99% on the cane; and the sucrose left in the molasses, which was 0·90% on the cane, or 7·27% sucrose in the juice. Attention may be drawn to the total loss of sucrose during manufacture, that is, the amount unrecovered in the form of sugars, which amounted to 18·34% of the total sucrose originally present in the cane, the various sources of this loss being distributed as follows: left in the bagasse, 7·99%; left in the filter-press cake, 0·49%; left in the final molasses, 7·27%; and unaccounted for, 2·59%. This last value should be decreased considerably in the case of future returns, if the conclusions of de Haan mentioned on page 397 are confirmed by other factory chemists. On the whole, these control values indicate a high state of efficiency in the factory, and at the same time thoroughness of work in the laboratory.

A further example of the extreme care with which chemical control is carried out in the sugar factories of Java as a whole is obtained by an examination of the so-called "unaccounted loss," which can be computed in two ways: (1) by deducting the sugar actually turned out from that calculated to be available (both values being, of course, in terms of the same grade of sugar, namely, "standard muscovado" of 96·5 polarisation); and (2) by deducting the accountable losses from the total losses as actually found by the analysis of the different products at the several stages of manufacture. Using these entirely different methods of calculating the unaccounted loss, the values obtained were 0·32% and 0·31% on the cane, which is a remarkably close agreement. Other chemical control results that have been published during the year under review emanate from Cuba,[90] Mauritius,[91] Hawaii.[92]

STARCHES AND GUMS.

Starches.—In this branch of the carbohydrate industry there is little to report. Reckitt & Sons, Ltd. and C. H. Hardy[93] in the manufacture of rice starch steep the grains in water for a few hours, and then grind them until 98% passes a 130 × 130 mesh silk sieve, water being added at the same time, so that the resulting paste contains 38–40% of solids, the starch being subsequently separated by centrifuging or decanting after further dilution. J. Effront and A. Boidin[94] utilise amylaceous residues from the starch, brewing, and oil industries by subjecting them to the action of bacterial diastatic enzymes[95] which exert their optimum effect in slightly alkaline solution, syrups being thus obtained after concentration of the converted liquid which are suitable for use in brewing and in the manufacture of sweets. V. G. Bloede[96] produces a modified starch by heating raw starch between 300° and 400° F. (149°–204° C.) for 30–60 minutes, the temperature and time of heating being so regulated that the product remains practically insoluble in cold water. R. W. G. Stutzke[97] desiccates and modifies a solution of starch by subjecting it in a finely divided state to a current of heated gas.

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[90] *Intern. Sugar J.*, 1920, 20, 225, 279, 438.

[91] *Bull. Soc. Chim. Maurice*, 1920, No. 41.

[92] *Intern. Sugar J.*, 1920, 471.

[93] E.P. 147,255; *J.*, 1920, 636A.

[94] E.P. 122,405; *J.*, 1920, 130A.

[95] E.P. 16,198 of 1914; F.P. 471,546; *J.*, 1915, 444.

Gums.—H. V. Dunham[98] prepared a " thickener " by dissolving Karaya gum in water containing about 3% of sodium bicarbonate (of the weight of gum), and dries the solution. He also produces two other compositions ; (1) by soaking the Karaya gum in water containing a small quantity of weak alkali, adding a lacteal fluid, and drying the mixture ; and (2) by mixing together soluble Karaya gum and soluble casein.

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[96] U.S.P. 1,324,332 ; *J.*, 1920, 202A.

[97] U.S.P. 1,320,719 ; *J.*, 1920, 37A.

[98] U.S.P. 1,334,356–1,334,358 ; *J.*, 1920, 380A.

DIRECTOR OF INDUSTRIES LIBRARY 9 JUL 1925 BENGAL.

FERMENTATION INDUSTRIES.

By Adam Tait and Louis Fletcher,

Chemists, Messrs. Wm. Younger & Co., Ltd., Brewers, Edinburgh.

Since the publication of last year's report the general trend in the fermentation industry has been a continuation of the endeavour to fill up the gap naturally formed by the exigencies of war. Progress unfortunately has been severely hampered by our very slow transition to normal peace conditions. Schemes for the reconstruction of the industry have been laid out, and the Research Fund of the Institute of Brewing is now an accomplished fact which it is to be hoped will assist the different branches which the Institute comprises to elucidate various problems and put the industry on a proper scientific foundation. If not perhaps following along the lines already well established by similar Continental institutions, a good deal might be learned from their experience. A comprehensive description of the Berlin Institute is given by F. M. Maynard (*J. Inst. Brew.*, 1920, **26**, 134). The French fermentation industries should benefit in the work of reconstruction by the assistance of the Commission which has been appointed for that purpose. A. Fernbach in an able article (*Ann. Brass. et Distill.*, 1918, **18**, 17) described the condition of the brewing, cider, vinegar, wine, and rum industries in France and pointed out the various schemes contemplated by the French Government with a view to the reconstruction of these industries which had been upset by enemy invasion during the war. On the other hand, while these schemes for reconstruction and research are in being, a small band of extremists is striving to bring about the total prohibition (in Scotland at least) of the manufacture and sale of exciseable liquor, but up to the present time (December, 1920) the voice of the Scottish people as expressed in the results of the local veto polls is emphatically against such undue interference with a perfectly legitimate industry.

Before commencing the main part of this year's report the writers wish here to tender their best thanks to Mr. J. S. Ford for his judicious criticism of the manuscript and for his able and valuable assistance in its compilation.

CHEMISTRY.

Evidence of the fascination of enzyme study is afforded by the number of contributions to the subject and, as in former years, a foremost position is given to the summarising of such work. There are no momentous discoveries to record, but the accumulation of data proceeds apace.

General Enzymes.

New ideas regarding the mode of action of hydrolytic enzymes have been introduced by M. Van Laer[1] which possess the element of originality, but whether or not the author's views are correct cannot be established without further work. Since the work is incomplete, a very abridged notice only will be given here. Van Laer's paper is another indication of the great importance that colloidal chemistry is assuming, and it is the study of the colloidal nature of enzymes which has apparently given rise to the present work. The action of hydrolytic enzymes is due, according to the author, to hydrogen-ions, for such actions can be produced by acids, *i.e.*, hydrogen-ions, without the agency of the enzyme itself. The solutions in which the enzymes act always contain hydrogen-ions at a low concentration, and as the ions are adsorbed by the colloidal particles, the hydrogen-ion concentration of the particle itself may thus be much greater than that of the solution as a whole, and as the particles are of specific adsorptive capacity (thus accounting for the specific action of enzymes), a substrate adsorbed by them comes under the influence of a comparatively high hydrogen-ion concentration and thus suffers hydrolysis, while other substrates not capable of being adsorbed by the enzyme remain unchanged. There are certain quantitative differences between hydrolysis by enzymes and by ordinary solutions of acids which can be explained by the colloidal nature of the enzymes which permit of hydrolysis taking place only in the adsorption zone of the enzyme particles. Thus the velocity of hydrolysis must be proportional to the concentration of the substrate in the enzyme particles and not in the solution. The concentration in the particles cannot be increased beyond a certain saturation limit, and further is not proportional to that in the solution. Enzymic hydrolysis, therefore, does not in general proceed according to the logarithmic law of unimolecular reactions, but the value of the velocity constant, K, may diminish or increase as the reaction proceeds, according to the relative proportions of enzyme and substrate, as was found by H. Van Laer[2] for the saccharification of starch by diastase.

The extraction of the enzymes of barley has been carried out by D. Maestrini.[3] Although the amylase of germinated barley is extracted by distilled water, the author found that by using water containing 0·003 mol.% acetic acid a more active solution was obtained, which was further augmented if the extraction was proceeded with for at least 6 hours. Protease is not extracted by distilled water, but extracts of high proteolytic value may be obtained by using 0·003 mol.% acetic acid. The lipolytic enzyme of barley can be detected only in the emulsion and not in the filtrate. His method of extraction applies equally in this case and highly active preparations have been obtained. For protease the optimal temperature is 45°–50° C., the enzyme being destroyed at 52°–55° C. and for lipase the optimal is 45° C. and destruction temperature 55° C. The same methods of extraction have been extended to the invertase of germinated barley dried at a temperature below 40° C. At least 6 hours' extraction at 30°–35° C. is necessary to obtain an active liquid. The enzyme acts best at about 50° C. and is destroyed at 55° C.

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[1] *Ann. Brass. et Dist.*, 1920, **19**, 19 ; *J. Inst. Brew.*, 1920, **26**, 598.

[2] *J. Inst. Brew.*, 1911, **17**, 513.

[3] *Atti R. Accad. Lincei*, 1919, **28**, II., 398 ; *J.*, 1920, 244A, 309A.

Incidental to some work in connexion with the process of desizing textile goods, involving the removal of starch present or embodied therein, S. H. Wakeman[4] has evolved a method for measuring the starch-liquefying powers of the enzymes employed. The problem is the removal of starch, not the production of sugar, consequently the Lintner method and its various modifications are not suitable. The author uses as a substrate a 2% paste of raw potato starch, 10 c.c. of which is maintained at 40° C. After adding a suitable amount of the enzyme solution the exact time required for liquefaction is noted. To assist the observation of the end-point the author uses neutral red as a stain for the starch. When the stage of hydrolysis as thus indicated is tested with iodine it is found to be identical with that at which no intense blue is obtained, showing that all the starch paste has been transformed to dextrins. Comparing the starch-liquefying powers of malt enzymes and the enzymes from *Aspergillus oryzæ*, commercially known as polyzime, the latter give a higher liquefying power while the malt enzymes show a higher Lintner value. After all, the method is not very original, although its application may be a little out of the ordinary, and further knowing the great difficulties attending the use of starch paste in such work, the writers wonder how much the results depend on the constancy of the nature of starch pastes.

As above stated, polyzime is the commercial name given to the preparation of enzymes resulting from the growth of *Aspergillus oryzæ* on media consisting chiefly of wheat bran. An account of the properties and also the chemical composition of such extracts is given by J. Takamine, jr., and K. Ashima.[5]

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[4] *J. Amer. Chem. Soc.*, 1920, **42**, 293; *J.*, 1920, 275A.

[5] *J. Amer. Chem. Soc.*, 1920, **42**, 1261; *J.*, 1920, 524A.

Further investigations have been made by H. C. Sherman and D. E. Neun[6] and later by H. C. Sherman, I. D. Garard, and V. K. La Mer[7] on the proteolytic activity of pancreatic amylase preparations. The first two authors[8] also Sherman and Schlesinger[9] have previously described the purification of high-grade commercial pancreatin, and the same method is again adopted except that in the final precipitation the usual 1 : 1 alcohol-ether mixture was replaced by a 2 : 1 mixture. The precipitate (A) was removed and a further precipitate (B) was obtained by adding ether to the filtrate. Precipitate (A) possessed a lower amylolytic and a higher proteolytic activity than did precipitate (B) and the amylolytic activity of (B) was higher than that of the usual amylase preparations. The authors recognise the difficulties due to the exceedingly unstable nature of the substances under purification and other causes, but they think it probable that a partial separation of a mixture of amylase and protease was accomplished. Since amylolytic activity deteriorates much more rapidly than does proteolytic activity under the conditions obtaining, the extra manipulation may thus cause a loss of such activity. The further possibility that there are enzyme-containing particles which possess both amylolytic and proteolytic activities is not excluded.

The paper by H. C. Sherman and F. Walker entitled "Influence of Aspartic Acid and Asparagine on the Enzymic Hydrolysis of Starch"[10] is a continuation of the work referred to in last year's report.[11] It is shown that small amounts of boiled, neutralised water extract of potato accelerate the action of the amylases of saliva and pancreatin and purified pancreatic amylase on alkali-washed potato, wheat, maize, and rice starches and on Lintner soluble starch, whilst the action of the vegetable amylases is not influenced by the addition of potato extract. The addition of neutralised aspartic acid or asparagine accelerates the action of saliva, pancreatin, and the purified pancreatic and malt amylases. Any possibility of the acceleration being due to changes to more favourable hydrogen-ion concentrations was eliminated by arranging that the substrate contained the optimum concentrations of sodium chloride and phosphate.

It is a practice in distilleries which use mucors as saccharifying agents, to liquefy the starch by cooking under pressure with a small quantity of hydrochloric acid. Regarding the amounts of acid required to produce the most satisfactory liquefactions in mashes P. Bettinger[12] gives experimental details. The same author in collaboration with Delaval[13] shows that the growth of mucor in mashes liquefied by amylase without the addition of acids is less than when a quantity of hydrochloric, sulphuric, oxalic, tartaric, phosphoric, succinic, or acetic acid is added. Acetic and succinic acids, which are excretory products, act favourably on growth at very low concentrations, but with increasing concentration they exert an inhibitive action much greater than can be accounted for by their degree of ionisation.

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[6] *Ibid.*, 1919, **41**, 1855 ; *J.*, 1920, 37A.

[7] *Ibid.*, 1920, **42**, 1900 ; *J.*, 1920, 700A.

[8] *J.*, 1918, 526A.

[9] *J.*, 1915, 627A.

[10] *J. Amer. Chem. Soc.*, 1919, **41**, 1866 ; *J.*, 1920, 37A.

[11] *Ann. Repts.*, 1919, **4**, 428.

Those fervid originators of the theory of the amylolytic properties of formaldehyde, G. Woker and H. Maggi,[14] recapitulate their evidence and also reply to recent criticisms.[15] They assume that the opponents to their theory kept their mixtures far too long, for the authors believe that the hydrolytic products are in time rebuilt into non-hydrolysable and non-reducing substances, such as the so-called "reversion dextrin." A similar re-building occurs when egg albumin is digested with papain (see Abderhalden's book).

It has been shown[16] that glycerophosphatase is very widespread in plant cells and in the tissues of ungerminated seeds. A. Nemec[17] finds the enzyme acts best in a medium having an acidity equal to 0·06 *N* and that the reaction is bimolecular.

The catalase of bacteria has been found by M. Jacoby[18] to obey the same reaction laws as the catalases previously studied.[19]

Although a great deal of work has been done on urease (extract of the soya bean), notably by H. P. Barendrecht and also by D. H. Wester, brief mention only can be made here. Barendrecht's publications[20] are of the continuous order and his investigations, which are being carried out in a thorough manner, cover the kinetics of urease action in both acid and alkaline solution, while the mathematical side of the problem is not neglected. Wester[21] has studied the factors which influence the conversion of urea into ammonium carbonate by means of urease. Other properties of the enzyme have also been investigated.

Yeast Enzymes.

The wide range of enzymes which are present in yeasts is very aptly illustrated by A. Fernbach.[22] Without contributing anything actually new to the subject, the author sets out in a most refreshing manner the various functions of each of the enzymes. He also makes numerous references to useful work of other investigators on the subject.

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[12] *Bull. Assoc. Chim. Sucr.*, 1919, **37**, 126 ; *J.*, 1920, 244A.

[13] *Ibid.*, 1919, **37**, 254 ; *J.*, 1920, 555A.

[14] *Ber.*, 1919, **52**, 1594 ; *J.*, 1920, 77A.

[15] *J.*, 1919, 433A, 508A ; see also *Ann. Repts.*, 1919, **4**, 422.

[16] *Biochem. Zeits.*, 1919, **93**, 94 ; *J.*, 1920, 244A.

[17] *Bull. Soc. Chim.*, 1920, **27**, 153 ; *J.*, 1920, 244A.

[18] *Biochem. Zeits.*, 1918, **92**, 129 ; *J.*, 1920, 168A.

[19] *J.*, 1918, 557A, 647A.

[20] *Proc. K. Akad. Wetensch.*, 1919, **22**, 29, 126 ; *J.*, 1920, 38A, 129A ; *Rec. Trav. Chim.*, 1920, **39**, 2 ; *J.*, 1920, 203A.

[21] *Chem. Weekblad*, 1919, **16**, 1442 ; *J.*, 1920, 38A.

An equation for the inverting power of yeast, within certain limits, is given by H. von Euler and O. Svanberg[23]:—

$$\text{Inversion} = \frac{\text{Inversion constant } k \times \text{grms. sucrose}}{\text{Number of yeast cells.}}$$

For a particular yeast which they designate as H, they observed a strongly marked temperature optimum of invertase formation between 26° and 30° C. From about 35° C. upwards the yeast exhibited no invertase formation. The maximum enzyme formation coincides very closely with the optimum activity of the invertase. The enzyme is slowly destroyed at an acidity greater than $p_{\text{H}}=2$, while a rapid production occurs at $p_{\text{H}}=6$–7, thus showing the dependence of the enzyme formation on the acidity.

T. Bokorny[24] contributes what is really a continuation of the work referred to in last year's report,[25] in which he described the effect of various antiseptics on the enzymic activities of yeast. In his present paper the author discusses the effect of different substances on the sucrase and maltase of yeast. Those without effect on sucrase are 0·25–0·5% oxalic or 2% acetic or lactic acid, even after 2 days' treatment; 0·5% soda solution is also without action on the sucrase of yeast. It is, however, slightly weakened by 0·1% hydrofluoric acid, while it is permanently destroyed by 0·5% sulphuric acid. Maltase is destroyed by air-drying yeast. In aqueous solution it is destroyed at 25° C., although it will remain active for a few days at a lower temperature. 5% alcohol weakens the enzyme and 0·1% thymol renders it inactive in a day. 1% soda destroys the enzyme in 4 days, although 0·5% soda is without any action, while a 0·02% solution of soda acts as a stimulant.

In connexion with the investigations of Euler and Berggren[26] and of Harden and Young,[27] H. von Euler[28] adduces new evidence to show that alcoholic fermentation by fresh top yeast is greatly accelerated by activators, presumably co-enzymes, which are present in aqueous yeast extract, and that the phenomenon is observed when the number of cells in the fermenting liquor undergoes no, or very slight increase. The activation of dry yeast by the co-enzyme is almost independent of the acidity of the solution in the region of $p_H = 3–7$. In contrast to Harden and Young, the author finds that the increase in the number of cells due to the addition of alkali formate never exceeds the experimental error involved in counting. On the other hand, it is shown that alcoholic fermentation by fresh top yeast is greatly accelerated by ammonium or alkali formate. E. Abderhalden,[29] who uses alcoholic yeast extract and whose methods differ from these of Euler in many respects, proves the stimulating action of his extract on the fermentation of carbohydrates by yeast. The same activating effect is also observed when expressed juice or dry yeast is used.

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[22] *Ann. Brass. et Dist.*, 1920, **18**, 161; *J. Inst. Brew.*, 1920, **26**, 325.

[23] *Z. physiol. Chem.*, 1919, **106**, 201; *J. Inst. Brew.*, 1920, **26**, 94.

[24] *Allg. Brau- u. Hopfenzeit.*, 1919, 881; *J. Inst. Brew.*, 1920, **26**, 531.

[25] *Ann. Repts.*, 1919, **4**, 426.

[26] *J. Chem. Soc.*, 1913, i, 145.

[27] *J. Chem. Soc.*, 1914, i, 237.

[28] *Z. techn. Biol.*, 1919, **7**, 155; *J. Chem. Soc.*, 1920, i., 463.

In a lengthy paper S. Lövgren[30] gives an account of the alteration of the inverting power of yeast by pre-treatment. The results are not of special importance.

A. Bach[31] has examined a method of Harden and Zilva for the detection of peroxydase in yeast (formation of a violet colour by yeast in a mixture of p-phenylenediamine and hydrogen peroxide). No positive results, however, could be obtained either with pyrogallol, guaiacol, or quinol. The violet colour occurs only in presence of acids, rising with the acidity to a maximum, when the amount of acid corresponds to 0·5 mol. per 1 mol. of p-phenylenediamine; with higher acidities the colour is not produced. It is concluded that the method is not practicable.

On the basis that enzymes are amphoteric electrolytes, K. G. Dernby[32] has examined the autolysis of yeast at various temperatures in the presence of electrolytes. The process consists in the degradation of the albuminous substances and the changes are wrought by a series of enzymes, operating simultaneously, contained in the simple yeast cell. The enzymes are analogous in type to those present in specific animal organs. The enzymes are identified as yeast pepsin, which degrades albuminous substances to peptone and has a maximum activity at $p_H = 4–4·5$; yeast tryptase which destroys gelatin, casein, Witte's peptone, and similar substances, and has a maximum activity at $p_H = 7·0$; yeast ereptase which degrades polypeptides to amino-acids and has a maximum activity at $p_H = 7·8$. The best hydrogen-ion concentration for the process is $p_H = 6·1$.

Starch.

The view held by Fernbach and Wolff[33] that an enzyme, amylo-coagulase, present in malt, is responsible for the coagulation of starch when small quantities of malt extract are added to starch solutions has been controverted by C. J. Lintner. The latter considers that starch in aqueous solution exists in the form of sols and gels, the former being a protective colloid for the latter. On adding a small quantity of amylolytic enzyme to a starch solution the highly dispersed sols are first attacked, and the gels, deprived of their protective colloid, are automatically coagulated. Experiments initiated by H. Sallinger[34] support the ideas of Lintner. By treating solutions of starch, where the degree of dispersion had been varied by certain means, with freshly filtered saliva and measuring the maltose produced and the amount of coagulation, under standard conditions, the author shows how greatly coagulation depends on the degree of dispersion of the starch solution. Further experiments are discussed which attack the amylocoagulase theory in other ways. That starch coagulation is only a subsidiary phenomenon of the saccharifying power of amylase is shown by the behaviour of starch solutions of different ages towards amylase. During the ageing of starch solutions sols become attached to gels originally present and are themselves converted into gels. That this conversion or ageing ("starch reversion") obeys certain laws is later shown by Sallinger[35] in his experiments with various kinds of soluble starch. The solutions in water were aged at 7° C. and at stated times 50 c.c. was removed and treated with 0·5 c.c. of saliva (ptyalin) and kept for 23 hours at the ordinary temperature. The precipitated gel was filtered and dried at 110° C. until of constant weight. If G is the weight of gel and t the time of ageing in hours it is found that the relationship between log G and log t is represented by a straight line and that numerically $G=gt^a$ where g and a are constants. The following values have been determined for different starches and it is shown that they are characteristic of the variety :—

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[29] *Fermentforsch.*, 1919, **3**, 44; *J. Chem. Soc.*, 1920, i., 349.

[30] *Ibid.*, 1920, **3**, 221; *Ibid.*, 1920, i., 462.

[31] *Fermentforsch.*, **1**, 197; *J. Inst. Brew.*, 1920, **26**, 100.

[32] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 23, 1; *J.*, 1920, 129.

[33] *J. Inst. Brew.*, 1904, 210; 1905, 190.

Potato starch 1	$g=4{\cdot}06$	$a=0{\cdot}445$
,, ,, 11	3·00	0·455
Wheat ,,	5·37	0·165
Barley ,,	11·17	0·214
Amylodextrin	3·51	0·521

The autolysis of starch by the action of saliva ash on starch solutions is causing a divergence of opinion between W. Biedermann[36] and H. Sallinger,[37] the latter's statements receiving support from Wohlgemuth[38] and Schultz.[39] Beyond recording, the controversy, the writers do not intend to make further comment.

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[34] *Koll. Zeits.*, 1919, **22**, 79 ; *J.*, 1919, 919A.

[35] *Koll. Zeits.*, 1919, **25**, 111 ; *J.*, 1920, 76A.

[36] *Fermentforsch.*, 1919, **2**, 458 ; **3**, 70 ; *J. Chem. Soc.*, 1920, i, 15, 291

[37] *Ibid.*, **2**, 449 ; *ibid.*, i, 15.

[38] *J. Chem. Soc.*, 1919, i., 361.

[39] *Fermentforsch.*, 1919, **3**, 72 ; *J. Chem. Soc.*, 1920, i., 291.

Fermentation.

With the object of establishing the dependence of the velocity of fermentation on the hydrogen-ion concentration, H. von Euler and S. Heintze[40] have investigated the fermentation of sucrose and dextrose by yeast at 28° C. using hydrochloric acid for producing the necessary acid concentrations. The p_H values were obtained by Sörensen's indicator method, and the velocity of fermentation was arrived at directly by measuring the volume of CO_2 evolved in a given time by 200 yeast cells. The maximum velocity occurs at $p_H=5{\cdot}0$ and this is also found after the addition of yeast water and asparagine to the fermentation mixture, although in these cases the velocity is much greater than in the absence of assimilable nitrogen. Oxalic acid and chromic acid in concentrations up to 0·025 *N* had no poisonous effect on fermentation as has been frequently stated. In solutions of hydrochloric acid up to 0·01 *N* the influence of the chlorine ions is unimportant, as also is the influence of the non-ionised molecules, but with weak organic acids the undissociated molecules play an important part.

Further experiments on the correlative formation of acetaldehyde and glycerol by the scission of sugar offer added proof of the possibility of the aldehyde stage in fermentation. While confining themselves to the limits of this report the writers will endeavour to give a short outline of the theory of alcoholic fermentation as enunciated by C. Neuberg and his co-workers, the outcome of investigations extending over a considerable period. C. Neuberg and J. Hirsch[41] have previously described what they term the "second and third forms of fermentation," the first being of course, the normal transformation of sugar into alcohol and carbon dioxide in accordance with Gay Lussac's equation. The "second form" is the now well-known transformation of sugar in the presence of sulphites, into acetaldehyde, glycerol, and carbon dioxide in accordance with the equation :—

$$C_6H_{12}O_6=CH_3CHO+CO_2+C_3H_8O_3.$$

If the fermentation is conducted in presence of alkaline substances such as carbonates, bicarbonates, phosphates, etc., which have no specific affinity for acetaldehyde, the latter is not fixed, but undergoes an enzymatic transformation into alcohol, acetic acid, and carbon dioxide. A summation of the whole series of reactions gives the following equation, which represents the authors' "third form" of fermentation :—

$$2C_6H_{12}O_6+H_2O=CH_3COOH+C_2H_5OH+2CO_2+2C_3H_8O_3.$$

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[40] *Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 2, 1-21 ; *J.*, 1920. 463A.

[41] *Biochem. Zeits.*, 1919, **100**, 304 ; through *Woch. Brau.*, 1920, **37** 21 ; *J. Inst. Brew.*, 1920, **26**, 259.

The following representation of the processes occurring in alcoholic fermentation is given by C. Neuberg and E. Reinfurth [42]:—

(i.) $C_6H_{12}O_6-2H_2O=C_6H_8O_4$ (the aldol of methylglyoxal).

(ii.) $C_6H_8O_4=2CH_2:C(OH)\cdot CHO$ or $2CH_3CO\cdot CHO$.

Thus the preliminary phase is the production of methylglyoxal which may be hydrated to form glycerol (iii), or it may be oxidised to the corresponding acid, *viz.*, pyruvic acid (v) :—

$$\text{(iii.)}\quad \begin{array}{l} CH_2:C(OH):CHO+H_2O+H_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2:C(OH):CHO+O \end{array} = \begin{array}{c} CH_2OH\cdot CHOH\cdot CH_2OH \\ + \\ CH_3\cdot CO\cdot COOH. \end{array}$$

The next stage is the breaking down of the pyruvic acid into carbon dioxide and acetaldehyde, the latter then being reduced to ethyl alcohol.

(iv.) $CH_3\cdot CO\cdot COOH=CO_2+CH_3COH$.

$$\text{(v.)}\quad \begin{array}{l} CH_3\cdot COH+\ H_2 \\ \qquad\qquad\quad\ | \\ CH_3\cdot CO\cdot COH+O \end{array} = \begin{array}{c} C_2H_5OH \\ + \\ CH_3\cdot CO\cdot COOH \end{array}$$

Considerable experimental data from which the theory has been deduced has been published from time to time, and the present communication contains further important confirmations. A paper by E. Zerner[43] dealing with the chemistry of alcoholic fermentation contains a report of the application of the Connstein-Lüdecke method for the production of glycerol in Austria. Some of his conclusions are at variance with those arrived at by C. Neuberg and E. Reinfurth.[44] Pyruvic acid, he states, in the presence of an equivalent amount of sulphite, is not fermented by yeast, and he further dissents from Neuberg's view that this acid is a precursor of acetaldehyde. Also, regarding the fact that glycerol does not increase in proportion to the added sulphite, he considers this is due to the slowness of the reaction between the acetaldehyde and sulphite, and that, in consequence, part of the acetaldehyde, together with an equivalent amount of glycerol, undergoes further transformations into alcohol and carbon dioxide. In reply to the latter statement Neuberg and Reinfurth[45] point out that Zerner overlooks the increasing alkalinity of the solution, and further the work of Kerb shows that the union is rapid. With regard to the other point raised by Zerner, they consider his conclusions are based on faulty experiment and later[46] they gave the results of experiments upholding their original statements.

On certain principles resulting from the studies already outlined,

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[42] *Ber.*, 1919, **52**, 1677 ; *J.*, 1920, 76A.

[43] *Ber.*, 1920, **53**, 325 ; *J.*, 1920, 276A.

[44] *J.*, 1920, 76A.

[45] *Ber.*, 1920, **53**, 462 ; *J.*, 1920, 345A.

[46] *Ber.*, 1920, **53**, 1039 ; *J.*, 1920, 524A

Neuberg[47] has elaborated two new biochemical methods for decomposing sugar. Collaborating with M. Ehrlich[48] he also proves that aldehydes accelerate the commencement of fermentation and are thus powerful stimulants to yeast—a view contrary to that of earlier workers who regarded aldehydes in general as being toxic to living cells and enzymes.

A. Fernbach and M. Schöen[49] in 1914 reported the production of a large amount of calcium pyruvate when alcoholic fermentation proceeded in presence of calcium carbonate. This is contrary to the experience of J. Kerb[50] who has found that pyruvic acid and its salts are more rapidly fermented by yeast than sugar itself. He thinks the previous workers must have used an impure ferment which produced lactate and then pyruvate.

ANALYSIS.

Consistency in the statement of analytical results is a worthy aim, and one that is neglected more than it should be. In the analysis of materials used in the fermentation industries alone, many examples could be cited where the need of reform is urgent. Many of the stated results lend themselves to ambiguity and also to misinterpretation. With regard to comparisons between British and Continental analyses the chief difficulty probably lies in the fact that the metric system is not of universal application in this country, so that before comparisons may be drawn much arithmetical labour is involved in recasting one set of figures.

Waters.

The foregoing remarks are peculiarly true of water analysis statements, and one would like to see a better agreement than at present exists. Recognition of the fact that any method of stating the composition of natural waters must be more or less arbitrary is not lost sight of, although this very fact is a plea for some sort of standardisation. It is not the intention of the writers to advocate any particular scheme—a matter really to be decided by a representative committee of experts—but they do think a consideration of the merits and demerits of methods employed by others will be of incalculable value. In Germany the official method now adopted is that recommended by H. Lüers.[51] The results are stated in terms of ions, expressed as millivals per litre, the millival being 1/1000 of the gramme-equivalent weight of an ion. Incidentally Lüers gives the working details for a set of volumetric methods whereby the analysis of waters may be carried out with speed and accuracy.

[47] *Chem.-Zeit.*, 1920, **44**, 9 ; *J. Inst. Brew.*, 1920, **26**, 169.

[48] *Biochem. Zeits.*, 1920, **101**, 239 ; *J. Inst. Brew.*, 1920, **26**, 560

[49] *J.*, 1914, **97**, 707.

[50] *Ber.*, 1919, **52**, 1795 ; *J.*, 1920, 76A.

[51] *Z. ges. Brauw.*, 1919, **42**, 209 ; *J.*, 1920, 275A.

Acidities.

The vexed question of acidity in brewing has stimulated the activity of several workers. F. Emslander[52] has published some interesting generalisations relating to the optimal hydrion concentration for the fermentative activity of brewer's yeast. He states that for brewer's yeast this optimum is $p_H = 4{\cdot}76 - 4{\cdot}46$, and in the case of other yeasts examined the reactions were less acid. In unfermented brewery wort the value is $p_H = 6{\cdot}5 - 5{\cdot}5$. In the case of dark beers made with water fairly rich in carbonates this value falls to $p_H = 4{\cdot}2$. By the production of acids, therefore, the yeast brings the hydrion concentration to approximately the most favourable one for its own fermentative activity. Since foreign yeasts prefer a less hydrion concentration, any circumstance tending to delay or prevent the yeast from attaining its own optimal concentration, *e.g.*, abnormally alkaline waters, too little yeast, low fermentation temperatures, etc., will accordingly react in favour of these foreign yeasts. P. Petit[53] considers Emslander's assumption that there is a specific optimum degree of acidity for all pale beers and another for all dark beers, is erroneous on account of the practical improbability of the conflicting influence of the different factors leading to the same final optimum. He urges the attainment of a simple, rapid, and accurate method of determining acidity in wort and beer so that the variations in acidity at the different stages of brewing could be studied, when it might be possible to trace the connexion between acidity and stability, haze, head, etc. The achievement of Petit's ideal method is to be cordially encouraged, and judging by this year's report is a desideratum engaging the attention of numerous chemists. The difficulties, however, in all work concerning these highly complex mixtures are enormous, and it is feared not sufficiently realised by many workers.

W. Windisch and W. Dietrich[54] have applied the method of Traube and Somogyi[55] to the measurement of the acidity of worts, beers, etc. In effect this method comprises the measurement of the surface tension of the wort relative to that of water, with a viscostagonometer, then adding a capillarily inactive salt of a capillarily active fatty acid, whereby they claim the surface tension of the wort is diminished owing to the liberation of free fatty acid equivalent to the wort acidity, and finally, determining the volume of standard alkali required to restore the original surface tension, *i.e.*, to neutralise the liberated acid. While admitting that the general idea of the method may be applicable under certain conditions, the writers question its validity with regard to worts and beers. The acidity of wort is not entirely due to primary phosphates; in fact the fatty and other acids derived from the hops, as also oxidation products of carbohydrates, represent a proportion of the acidity not to be neglected, while in a beer the acidity due to fatty and other acids is considerably higher. Further the acidity of worts and beers is not a simple, but an equilibrium acidity, the worts and beers possessing both potential acidic and basic properties. That the authors are aware of the presence of fatty acids in worts and beers is shown by the fact that they ascribe certain results reported in Part IV. of their treatise to the presence of capillarily active fatty acids, but these they consider are too small to interfere seriously with their method, a view to which the writers cannot subscribe.

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[52] *Z. ges. Brauw.*, 1919, **42**, 127 ; *J.*, 1920, 129A (also *J.*, 1914, 212).

[53] *Brass. et Malt.*, 1920, **9**, 337 ; *J. Inst. Brew.*, 1920, **26**, 263.

[54] *Woch. Brau.*, 1919, **36**, 189 ; *J.*, 1920, 128A.

[55] *J.*, 1915, 511.

For estimating the total volatile acidity in fermented products M. G. Hinard[56] proposes a modification of Pasteur's method, which in brief comprises the repeated distillation of the product, re-making to original volume before each distillation. Hinard simplifies the operations by using graphic methods of extrapolation to avoid unnecessary repetitions of the process. By these means he proposes to replace Duclaux's method, the limitations of which he describes. The imperfections of Duclaux's method have long been realised, as a perusal of the literature of the last decade will show. The many efforts of improvement include a series of notable contributions from H. Droop Richmond.[57] As a matter of experience the writers would not prefer Hinard's modification to Duclaux's method or suitable improvements thereof, and again insist on the necessity of elucidating the complex nature of these liquids before proceeding further with methods for their estimation.

General.

An interesting note on the determination of amylolytic activity has appeared by E. I. Rosenblum.[58] The object of the work is to prove the dependence of the amylolytic activity on the hydrogen-ion concentration of the substrate, a point which is already well known. His method of adjusting the "neutrality" is not a new one, the writers having employed similar methods for the past 14 years. The paper, however, may serve to emphasise the great importance of the matter. Rosenblum refers to the early work of certain authors, but he has singularly neglected to note the later work of the same and many other writers, which has a direct bearing on the subject. In the main, such work is published in the *Journal of the Institute of Brewing*, a natural place to look for information on the subject. It seems a pity that for his amylolytic activity determinations Rosenblum should not have selected the method already standardised in this country instead of that of Harrison and Gair[59] which has been shown by Ling[60] to be open to various objections.

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[56] *Ann. Chim. Analyt.*, 1920, **2**, 239; *J.*, 1920, 669A.

[57] *Analyst*, 1908, **33**, 305.

[58] *J.*, 1920, 311T.

The iodometric method for the estimation of the copper reduction in the determination of amylolytic power as described by J. T. Flohil[61] does not suggest any improvements over the older and well-known volumetric methods of A. R. Ling and G. Bertrand.

A. Slator[62] describes an apparatus specially designed to estimate the total amount of carbon dioxide formed when sugars are fermented by yeast. It was subsequently found to be of general use and can be employed in most cases where it is necessary to estimate this gas. Experiments are detailed showing that it may be used to estimate the fermentable carbohydrate content of an ordinary wort and also to ascertain the presence or absence of a particular enzyme in yeasts by using certain specific sugars as substrate.

The values for the original gravities of beers as calculated by Balling's original formula are not strictly accurate (see Schönfeld[63]), and experiments by F. Harder[64] were designed to discover if loss of alcohol during fermentation is responsible for the discrepancy. His results show that such is not the cause of the difference. The important and exhaustive work of Thorpe and Brown when compiling their report on "The Determination of the Original Gravity of Beers by the Distillation Process" shows the many minor but important details which must be considered in working out any general formula. A process which can be used for determining the alcohol content of beer or wine by using electrical conductivity methods has been recommended by I. M. Kolthoff.[65] A device for testing for, and it is claimed, quantitative estimation of alcohol is described by S. Waldbott.[66] By taking the time during which the alcohol vapour expelled from beer will burn, a measure is obtained of the alcoholic strength of the liquid. This method the writers class as retrogressive. It is reminiscent of the days when spirits were tested by the gunpowder method and ale by the leather breeches standard.

For detecting the presence of brewer's yeast in pressed yeast E. Vautier[67] proposes Herzfeld's method as a qualitative test.

[59] *Pharm. J.*, 1906, **77**, 94.

[60] *Chem. and Drug.*, 1910, **76**, 52 ; *J. Inst. Brew.*, 1910, 567.

[61] *J. Ind. Eng. Chem.*, 1920, **12**, 677 ; *J.*, 1920, 580A.

[62] *J.*, 1920, 149T.

[63] *J.*, 1910, 292 ; 1911, 762.

[64] *Woch. Brau.*, 1919, **36**, 277 ; *J.*, 1920. 203A.

[65] *Rec. Trav. Chim.*, 1920, **39**, 126 ; *J.*, 1920, 203A.

[66] *J. Ind. Eng. Chem.*, 1920, **12**, 690 ; *J.*, 1920, 580A.

[67] *Ann. Chim. Analyt.*, 1919, **1**, 345 ; *J.*, 1920, 38A.

The principle of the method depends upon the fact that raffinose is not attacked by pressed yeast, whilst it is easily fermentable by brewer's yeast. Arising from the same observation Bau suggests the following quantitative test :—10 c.c. of 1% raffinose solution +0·4 g. of yeast is placed in each of three test tubes which are maintained at 30° C. After 24 hours one tube is tested by boiling 3 c.c. of a filtered portion with 1 c.c. of Fehling's solution for 5 minutes; if the blue colour is not destroyed the yeast contains at least 10% of brewer's yeast. If raffinose is still present, as shown by the destruction of the Fehling's solution, a second tube is examined in the same way after 48 hours, the non-discharge of the blue in this case indicating the presence of about 5% of brewer's yeast. A blue coloration in the third day's test, *i.e.*, after 72 hours' incubation, denotes 1% of brewer's yeast.

As an item of interest more than of practical utility the experiment of J. E. Abelous and J. Aloy[69] is worth recording. They passed a solution of 5 g. of saccharose in 100 c.c. of water through a Richardson atomising apparatus five times, thereby increasing the content of H and OH ions by converting the water into a fine spray, with the result that invert sugar was formed to the extent of 0·6 g.

Various substances were tried by J. S. McArne and A. N. Thurston[70] for preventing fermentation when drawing samples of " near " beer for analytical purposes. Sodium bisulphite and boric acid are useless. Sodium benzoate is unreliable, but mercuric chloride and salicylic acid are quite satisfactory. Salicylic acid is recommended as it is non-poisonous and cheaper than mercuric chloride. Salicylic acid, of course, has been used by our Revenue authorities for many years.

To obviate the drawbacks of sodium chloride used for the yellow light in polarimeter work, Dupont in 1897[71] proposed a mixture of salt and trisodium phosphate. This is revived by L. Guglialmelli,[72] who finds it works very satisfactorily. For its preparation, 1 g.-mol. of disodium phosphate is dissolved in water and treated with 1 g.-mol. each of sodium hydroxide and chloride. The solution is evaporated to dryness and the residue fused

F. Lucius[73] states that dextrose may be estimated in presence of lævulose by heating with hydrochloric acid in a boiling water-bath for 7 hours. By this treatment the rotatory power of lævulose is destroyed and the dextrose may be determined polarimetrically after cooling, neutralising, and making to a known volume. The

[69] *Comptes rend.*, 1919, **168**, 1125.

[70] *J. Ind. Eng. Chem.*, 1920, **12**, 689 ; *J. Inst. Brew.*, 1920, **26**, 483.

[71] *J. Chem. Soc.*, 1897, ii, 77.

[72] *Anal. Soc. Quim. Argentina*, 1918, **6**, 497 ; *J. Chem. Soc.*, 1920, ii., 444.

[73] *Z. Unters. Nahr. Genussm.*, 1919, **38**, 177 ; *J.*, 1920, 127A.

writers doubt the accuracy of this method, for, apart from other considerations, it has long been known that dextrose is not immune from attack when heated with hydrochloric or sulphuric acid.

A test for the presence of methyl alcohol in spirits given by P. Hasse[74] is essentially the same as that already published by E. Salkowski (see *Ann. Repts.*, 4, 420). Lemoigne[75] has published the details of a test for acetyl methyl carbinol, sensitive to a dilution of 1 in 1,000,000, which serves to differentiate certain groups of bacteria. The test is applied to bacterially decomposed sugar and the carbinol is readily detected among the fermentation products, the reaction not being given by any of the other products. With reference to fermentations conducted in presence of calcium sulphite, C. Neuberg[76] gives a test for acetaldehyde: 3 c.c. of liquid without filtration is treated with 0·5 c.c. of 4% sodium nitroprusside solution and 2–3 c.c. of 3% piperidine solution. In presence of acetaldehyde a deep blue coloration is produced, while with normal fermentation products no change occurs. C. A. Rojahn[77] has tried Zeisel's [78] method for the estimation of fermentation glycerol. The method is not applicable owing to the presence of trimethyleneglycol which develops di-iodopropane; this passes over more or less completely with the isopropyl iodide.

BARLEY AND MALT.

J. O'Sullivan[79] has published some interesting work on the influence of the temperature, concentration, duration of the mash, and slackness of malt on the starch products of the extract of malt. At the outset he shows by experiment that invertase is not present in malt and concludes that the greater extract and the higher cupric-reducing power of the cold water extract of malt over that obtained by the standard method using alkaline water are due to the solution of starch granules and not to the inversion of sucrose. By determining the specific gravities of the cold water extract (using alkali) and the ordinary mash extract, and the cupric-reducing powers of these extracts, the composition of the starch transformation-products and the amount of starch in the malt can be calculated. A slight correction for the albuminoids is necessary. The dextrin can be found from the above by deducting the maltose from the starch products, allowance being made for hydrolysis (1 g. starch=1·055 g. maltose). The "transforming power" of the malt is expressed by the percentage of starch which is converted into maltose. By fermenting the mash extract with yeast and determining the degrees fermented the percentage of extract fermented is obtained. From the degrees of gravity of the cold water extract fermented together with the degrees corresponding to the maltose found in the mash extract the percentage fermentable is deduced. The amount of starch products fermented is obtained by deducting the degrees of gravity of the cold water extract fermented from the total degrees of the mash extract fermented; the difference is due to the degrees of gravity corresponding to the starch products fermented.

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[74] *Pharm. Zentralh.*, 1920, **61**, 177; *J.*, 1920, 345A.

[75] *Comptes rend.*, 1920, **170**, 131; *J.*, 1920, 203A.

[76] *Woch. Brau.*, 1919, **36**, 292; *J.*, 1920, 276A.

[77] *Ber.*, 1919, **52**, 1454; *J.*, 1920, 77A.

[78] *J.*, 1902, 992.

[79] *J.*, 1920, 22T.

The above is a brief account of the method used by the author and gives some idea of the amount of work involved when it is seen how many extracts and mashes were examined. It is outside the scope of this report to enter into details regarding the results, and the reader is referred to the Journal where tables and the conclusions arrived at may be studied.

P. Petit[80] shows the fallacy of reducing the malting loss at the expense of restricted germination where the resultant malt is to be used for brewing purposes. Such a procedure will yield a malt imperfectly modified with regard to soluble nitrogenous substances. As the malt is likewise deficient in proteolytic activity the conversion of the imperfectly dissolved proteins into completely soluble degradation products by " protein rest " is incomplete. Pre-mashing will partially overcome this, but the nitrogenous substances by this procedure will not be in stable solution, contributing a doubtful value to flavour and head formation, and imparting grave risks of protein haze in the finished beer. F. Tombeur[81] has studied the changes produced in starch and nitrogenous substances during malting. The methods of malting as advised by the author are not those calculated to produce the best results from the barley and, moreover, the results obtained from a single malting cannot be used as a basis for arriving at definite conclusions.

Continuing his work on the titration of barleys in stages, A. Reichard[82] gives data which bear out Delbrück's suggestion[83] that the types of barley most liable to rapid heating on the floor are those with small corns, rich in proteins and with thin husks. H. Langkammerer and H. Leberle[84] give an account of investigations carried out on a number of samples of malt differing greatly in character and in some cases showing abnormal features, by applying a modification of Sörensen's " formol " titration method.

[80] *Brass. et Malt.*, 1919, **9**, 241; *J.*, 1920, 345A.

[81] *Bull. Assoc. Anc. Élèves de Louvain*, 1920, **20**, 72; *J.*, 1920, 461A.

[82] *Z. ges. Brauw.*, 1919, **42**, 223; *J.*, 1920, 275A.

[83] *J. Inst. Brew.*, 1902, **8**, 513.

[84] *Z. ges. Brauw.*, 1919, **42**, 236 *seq.*; *J.*, 1920, 202A.

Three extracts were made: (i) An extract of malt, the enzymic activity of which had been previously destroyed by alcohol; (ii) ground malt previously digested at a favourable temperature for proteolytic activity, and (iii) malt extracted as in the method used in malt analysis in Germany. The "formol" nitrogen was determined in each case and also the hydrion-concentration. The worts were fermented in the laboratory and in the resultant beers the acidity by titration, hydrion-concentration, and "formol" nitrogen were determined, the acid titration being carried out by Lüers' method to a $p_H=9{\cdot}18$. The authors make some interesting remarks regarding the titration with an end-point at $p_H=9{\cdot}18$. They state that this gives a fairly accurate measure of the total amount of potentially acid substances present, but maintain that it is a very unsatisfactory means of estimating active acidity. For this purpose it is better to determine the hydrion-concentration, or at least to use an indicator having an end-point near absolute neutrality. As a result of their research the authors consider that the "formol" titration method is not only valuable in scientific researches but may also throw some light on the question of the character of malt. In the writers' opinion, the alcohol treatment (i) mentioned above, will do a good deal more than destroy enzymic activity; it is certain that the acid equilibrium in the extract after such treatment will not be the same as existed in the malt.

E. J. Russell[85] has investigated the results of electrolytic treatment of oat and barley seeds, a method which is claimed to increase the weights of crops, but considers that this treatment is of less value than judicious manuring. D. Atanasoff and A. G. Johnson[86] find that seeds of various cereals, including barley, if of good quality and well-dried, may be heated for 30 hours at 100° C. without losing their power of germination. This treatment also destroys certain fungoid pests and impairs the activity of others.

A. Fernbach[87] in a comprehensive review on germination discusses our present knowledge of the subject and makes valuable suggestions for further investigations with a view to the reduction of malting loss etc.

HOPS.

A. H. Burgess[88] gives a detailed account of investigations carried out at Wye College in connexion with hop production. His *résumé* of the experimental work carried out is given in detail under various headings. Many instructive tables and charts are included in the paper, and in addition the author offers a few suggestions for future work. The results of work continued by E. S. Salmon[89] are published in the form of a report.[90] In addition to the experiments carried out last year there is a new feature contributed by G. T. Cook and H. Harman on the question of the suitability of certain of the new varieties for dry-hopping purposes. This practical side of the subject is quite a useful addition.

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[85] *J. Ministry Agric.*, 1920, **26**, 971; *J.*, 1920, 291A.

[86] *J. Agric. Res.*, 1920, **18**, 379; *J.*, 1920, 243A.

[87] *Ann. Brass. et Dist.*, 1919, **18**, 113; *J. Inst. Brew.*, 1920, **26**, 262.

[88] *J. Inst. Brew.*, 1920, **26**, 429.

J. V. Eyre, E. S. Salmon, and L. K. Wormald[91] have made further investigations into the ammonium polysulphide wash for the destruction of powdery mildew of hops.[92] The authors describe a method of preparing a stock solution of such a strength that when diluted with 200 times its volume of water it yields a wash which is fungicidal against the powdery conidial stage of hop mildew.

An attempt is made by H. Lüers and A. Baumann[93] to estimate the hop bitter acids by measuring the surface tension of these acids. Some experiments were tried to study the changes in these acids during boiling. The authors show by surface tension measurement that α-bitter acid, the so-called humulone of hops, lowers the surface tension of water. The important point of head retention in beer is due to reduction of surface tension, and in further work[94] on this subject the authors show that α-bitter acid is responsible to a great extent for the production of stable foam in beer.

BREWING.

In the manufacture of a stable pale beer H. Lüers[95] states that a better product with regard to flavour, colour, stability, etc., can be obtained if the mash or wort is acidified by means of *Bacillus Delbrücki* (Windisch, *J.*, 1913, 986). The details and conditions of working are given. The interest in the process must of needs remain largely theoretical, however, for the loss of extract involved in acidification makes it too costly for ordinary use.

By using ultra-filters of varying porosity W. Windisch and V. Bermann[96] have separated from beer wort the colloidal particles which give rise to head-retention, and have further been able to gain an approximate measure of the degree of fineness such particles possess. The residue from an ultra-filtration, if washed free from sugars and salts, dried, and then treated with water, is divided into soluble or reversible and insoluble or non-reversible colloids. If the soluble portion is added to the ultra-filtrate which is now

[89] See *Ann. Repts.*, 1919, **4**, 433.

[90] *J. Inst. Brew.*, 1920, **26**, 554.

[91] *J. Bd. Agric.*, 1919, **26**, 821 ; *J.*, 1920, 80A.

[92] See *Ann. Repts.*, 1919, **4**, 434.

[93] *Z. ges. Brauw.*, 1920, **43**, 65 ; *J.*, 1920, 462A.

[94] *Koll. Zeits.*, 1920, **26**, 202 ; *J.*, 1920, 498A.

[95] *Z. ges. Brauw.*, 1920, **43**, 51 ; *J.*, 1920, 462A.

[96] *Woch. Brau.*, 1920, **37**, 309 ; *J.*, 1920, 462A.

only able to give an abundant, but non-persisting froth, it is found to regain its power of head-retention. A further examination of these reversible colloids showed that they were composed in part of a non-coagulable protein which is capable of producing, but not retaining, head, but chiefly of a non-protein substance, of a carbohydrate nature, which rendered the head persistent. The head-producing proteins have a high capillary activity, while the non-proteins which give a persisting head have a low capillary activity. The authors have employed the " iron value " (analogous to the " gold value " of Zsigmondy, *J.*, 1902, 192) for characterising the colloids which are responsible for head-retention. This " iron value " is measured by the concentration of sodium chloride solution required for just producing turbidity or flocculation of a ferric hydroxide sol in presence of the colloid. This question of head-retention has also been investigated by H. Lüers, K. Geys, and A. Baumann,[97] who find that the size of the colloidal particles plays an important part. They collected the foam from war beers of 4·5% wort gravity and also from export beers of 11% gravity. The foam obtained was allowed to settle and the " foam beers " compared with the original beers. There was practically no difference in the alcohol content. In general there was more total nitrogen in the " foam beers," but considerably less amide-nitrogen. The total acidity was somewhat higher in the " foam beers " and the volatile acidity distinctly so, from 2–10 times as great. The surface tension was lower in all cases. From these and various other observations with regard to viscosity, esters, higher alcohols, etc., the authors conclude that certain substances appear to be detrimental to head formation.

F. M. Maynard[98] advocates the production of a *true* lager beer for the foreign market to replace the German product that was exported to our Colonies before the war, at the same time pointing out that such a beer will need to be in every respect as good an article as the continental. He gives an account of the various processes in a modern lager beer brewery, including malting, mashing, fermentation, and lagering or storing, giving many tables of figures. In addition the question of cask pitching and washing, and bottling are detailed. Interesting diagrams showing the ratio of alcohol to malt extract in stouts and ales made in this country compared with various lager beers brewed in Germany are given.

Lowitz[99] recommends the grinding of hops to a fine state of division before adding them to the wort ; in this way the extraction is rendered so complete that the hop-rate may be reduced considerably, and the time of boiling curtailed, whereby a saving of

[97] *Z. ges. Brauw.*, 1920, **43**, 185, 193, 201 ; *J.*, 1920, 607A.

[98] *J. Inst. Brew.*, 1920, **26**, 485.

[99] *Brass. et Malt.*, 1920, **10**, 60 ; *J. Inst. Brew.*, 1920, **26**, 476.

fuel also can be obtained. In the writers' opinion this is a very striking example of false economy because the time of boiling, with a consequent increase of wort acidity, cannot be overlooked.

W. Windisch[100] gives some advice, based on experience on the steeping and malting of oats for brewing purposes, and also on the use of this material in the mash-tun, by comparing the relative saccharifying powers of oat malt and barley malt. He finds that flavour and head-retention of oat malt beer is quite satisfactory and the palatefulness is even better than in beer made from barley malt. The only drawback, according to Windisch, in the use of oat malt is that it gives less extract than barley malt, but no doubt his conclusions are largely influenced by conditions in Germany as to the supplies of barley.

The degeneration of yeast in the manufacture of war-beers was evident in many continental breweries, but the reason for this was not so easily ascribed. While investigating the cause of this trouble E. Moufang[101] states that he has proved the presence of a substance which he has termed "testilupine," since it was found to be a compound of testine from the husk of barley and lupuline from hops. This substance, which the author has isolated in quantity, retards the action of yeast by adhering to its surface. It was found that those malts which had been made with a view to decreasing or transforming the testine, yielded worts most satisfactory for low-temperature fermentations. The author suggests that a new criterion for malts has been established. He details a method of steeping with alkaline water which reduces the amount of testine, and also improved methods of boiling the wort produced from such malt. This process consists in "boiling under open pressure." This means that although the pressure is kept as high as 2 atm., there must also be a continual escape of steam, which removes the various decomposition products. He finally states that beers produced under this system are richer in non-assimilable nitrogenous substances, and these beers have better "heads" and are more stable than other beers. The present writers think that Moufang's isolation of the so-called "testilupine" is of more than mere passing interest, but are at variance with his final conclusion regarding the stability question.

Low-gravity beers.

Restrictions still being in force in this and other countries, it is not surprising that further study should have been expended on the peculiarities in the production of beers of a much lower gravity than those made prior to 1914.

[100] *Woch. Brau.*, 1920, **37**, 56; *J. Inst. Brew.*, 1920, **26**, 421.

[101] *Brewing Trade Review*, 1920, **34**, 346.

C. G. Matthews[102] gives a very interesting and instructive *résumé* of the requirements of yeast generally, its sustenance with reference to the influence of acids and the brewing of low-gravity beers. The author claims no novelty for his communication, but it gives a very good account of the main problems confronting brewers at the present time.

H. Will[103] records different causes of hazes in low-gravity beers due to wild yeasts, sarcina, and rod bacteria. The same author gives an account[104] of the results of observations on the keeping quality of war-beers of original gravity 1014–1016. He found that thin beers were more liable to go hazy than normal beers, although the time of the appearance of a haze or turbidity varied with the different samples which he examined. Will considers that if beers of this nature remain brilliant for about a week, they could be classed as satisfactory. With regard to the stability of low-gravity beers R. Heuss[105] recommends stringent measures being taken to ensure the use of a sufficiency of antiseptic during manufacture, and advocates a rigid bacteriological control at all stages of the process.

Brewing Materials.

Owing to the unavoidable lack of transport at the present time and the resultant necessity for storing raw materials, various precautions have had to be instituted to prevent deterioration of these materials. Moisture is perhaps the most important factor and J. S. McHargue[106] has found this to be the case in the deterioration of maize. Maize when dried to about 12% of moisture will keep in a satisfactory state for quite a long time provided access of damp air is excluded. If this precaution is overlooked the moisture content rapidly increases to 17–20% when moulds will soon develop and cause a rapid deterioration of the oil, sugar, and starch contained in the germs. Similar effects were noted when the maize was kept in the ground state under these conditions.

The Grain Pests (War) Committee, appointed by the Council of the Royal Society to investigate into the damage done to grain by insects, showed the necessity of air-tight storage. A very full report of the conclusions arrived at by this committee is given in the Journal of the Institute of Brewing.[107]

With regard to the storage of Cuban raw sugars N. Kopeloff

[102] *J. Inst. Brew.*, 1920, **26**, 239.

[103] *Z. ges. Brauw.*, 1919, **42**, 199 ; *J. Inst. Brew.*, 1920, **26**, 176.

[104] *Z. ges. Brauw.*, 1919, **42**, 191 ; *J. Inst. Brew.*, 1920, **26**, 176.

[105] *Brass. et Malt.*, 1920, **10**, 168 ; *J. Inst. Brew.*, 1920, **26**, 564.

[106] *J. Ind. Eng. Chem.*, 1920, **12**, 257 ; *J.*, 1920, 381A.

[107] *J. Inst. Brew.*, 1920, **26**, 414.

and H. Z. E. Perkins[108] give the results of a combined chemical and bacteriological investigation into the causes of the loss in cane sugar-content. The following estimations were made before and after storage: polarisation, moisture, reducing sugar, and ash, also the number of bacteria and moulds per grm. of sugar. The authors have determined the "factor of safety" which is calculated from the formula,

$$\text{"Factor of safety"} = \frac{\text{Moisture percentage}}{100 - \text{polarisation}}$$

They found a gradual decrease in this "factor of safety" on storage for different lengths of time, due to an increase of reducing sugars and moisture content with a decrease in the polarisation figure. With regard to the bacteriological side of the question a definite relationship seems to exist between the moisture-content and the number of organisms present.

The roasting of barley and malt, though a comparatively small industry connected with brewing dark beers, is one of some importance, and to those interested the writers would recommend a perusal of the description of the process given by G. Valentine.[109]

YEAST.

The current year embraces an unusual number of publications relating to yeast, from the biological, chemical, and technical standpoints. The more important, excluding that by Lampitt (*cf. infra*), are written by men who in the past have devoted considerable attention to the manifold problems connected with yeast. The particular papers referred to here, however, are not of outstanding original merit, although their value as summaries and commentaries is not to be disparaged. Such a paper is that by A. Klöcker,[110] whose work on the assimilative capacity of yeasts for sugar is prefaced by a lengthy discussion of previous researches on the subject. In arranging his own work Klöcker has taken advantage of the experience of his contemporaries and has tried to eliminate the pitfalls which he has detected in their methods. His results are summarised in a table which shows at a glance the assimilative capacities of several species of yeast for different sugars, with three separate sources of nitrogen.

"The nitrogen metabolism of *Saccharomyces cerevisiæ*" is the subject of the paper by L. H. Lampitt[111] referred to above. While there is no doubt that this paper is a valuable contribution to the subject, many of the results obtained with the artificial nutrient solutions, naturally selected for such work, are greatly at variance with the results obtained in industrial practice. In the experience

[108] *J. Ind. Eng. Chem.*, 1920, **12**, 555; *J.*, 1920, 583A.

[109] *J. Inst. Brew.*, 1920, **26**, 573.

[110] *Comptes rend. Carlsberg*, 1919, **14**, 1; *J. Inst. Brew.*, 1920, **26**, 57.

[111] *Biochem. J.*, 1919, **13**, 456; *J.*, 1920, 669A.

f the writers the use of asparagine or other acid amides as a ource of nitrogen in fermentation experiments, without due rovision of a sufficiency of " buffer salts " or other amphoteric ubstances to neutralise the acid derived from such nitrogenous ompounds, leads to results which cannot be considered normal nd certainly provide dangerous data for the deduction of far-eaching general conclusions. Unless provision is so made, the nain controlling factor in such fermentations may be acidity.

L. Lindet[112] deals with the influence of the vegetative function f yeast on the yield of alcohol, and continues the work reviewed n last year's report.[113]

A brief reference is all that need be made to the paper by T. Bokorny[114] since he occupies himself almost exclusively with Munich brewery pressed yeast and includes much work already published under different titles. For a similar reason the writers leem it unnecessary to devote much space to the contribution[115] mbodying the work of H. Zikes,[116] though the work is interesting, s the titles to the sub-sections show—(i) Experiments on the influence of wort concentration on the fermenting and reproductive apacity; (ii) the effect of concentration on yeast reproduction; iii) the effect on the morphology of the yeast—its glycogen and fat content. Unfortunately Zikes took as his standard wort one with a gravity of 1013, obtaining weaker ones (down to 1001) by dilution. The results therefore are not applicable to this country where the conditions of concentration obtaining are so different. In another communication H. Zikes[117] has collated the statements in literature and the results of his own experiments relating to the influence of temperature on the various activities of yeast. These include (A) Vegetative growth, budding capacity and generative period, (B) spore formation, (C) film formation, (D) fat formation, (E) glycogen formation.

Some figures concerning the growth of yeast in alkaline solutions are given by H. von Euler and O. Svanberg.[118] They have determined the maximum alkalinity at which different types of yeast will grow. For a Frohberg bottom yeast it is $p_H=7\cdot7$–8, while a distillery top yeast (S.B. 11.) showed a decided growth at $p_H=7\cdot3$. For *Saccharomyces ellipsoideus* and *Pseudosaccharomyces apiculatus* respectively it is $p_H=7\cdot9$ and $p_H=7\cdot6$. *Aspergillus niger* withstood an alkalinity of $p_H=9$ as its highest limit.

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[112] *Ann. Brass. et Dist.*, 1919, **18**, 85; *J. Inst. Brew.*, 1920, **26**, 172.

[113] *Ann. Repts.*, 1919, **4**, 439.

[114] *Pflügers Arkiv*, 1916, **164**, 203; through *Physiol. Abstr.*, 1916, **1**, 453; *J. Chem. Soc.*, i., 350.

[115] *Z. ges. Brauw.*, 1920, **43**, 188; *J. Inst. Brew.*, 1920, **26**, 480.

[116] *Zentr. Bakt.*, 1919, **49**, 174; *ibid.*

[117] *Zentr. Bakt.*, II, 1919, **49**, 353; *J. Inst. Brew.*, 1920, **26**, 530.

[118] *Arkiv Kemi, Min., Geol.*, 1918-1919, **7**, No. 11, 1; *J.*, 1920, 245A.

Euler and N. Florell[119] state that there are two ways in which dyes are absorbed by yeast. The more usual phenomenon is that of surface adsorption in which case the stain can only be detected in reflected light. The other case is where the dye is absorbed into the interior of the cell and retained therein, the stain being visible under the microscope. In both cases the absorption is influenced by such factors as hydrogen-ion concentration, temperature, concentration of the dye, and the presence of fermentable sugar in the solution. Staining with certain dyes impairs the fermenting power of yeast. The staining or non-staining of cells with, say, methylene blue is not conclusive evidence of their being dead or alive, as the writers know from experience. In 1914 Matthews[120] published a useful paper on the staining of yeast cells by methylene blue. Reference should also be made to the contribution of E. Schlichting and H. Winther.[121]

According to P. Thomas[122] the content of tryptophan in caseinogen is approximately 1·7—1·8%. The protein substance from yeast cerevisin contains about 2·3%, and is the substance containing the highest percentage of tryptophan which is known. It also contains a high percentage of lysine, a fact which places this protein in a class by itself.

I. S. MacLean and E. M. Thomas[123] describe the nature of yeast fat and give a description of the methods employed for its preparation and examination. The sources were baker's yeast, brewery yeast, and a pure culture yeast. The paper contains much valuable information. Regarding the formation of fat in yeast on solid media, P. Lindner and T. Unger[124] suggest that the abnormally high production of fat globules in the superficial cells of yeast cultures on solid media, is due to the influence of alcohol vapour produced by the underlying cells. They also present a tabular record of the microscopical appearance of cultures of the numerous yeasts in the Versuchs- und Lehranstalt für Brauerei collection in Berlin.

P. Thomas[125] states that yeasts under certain conditions are capable of utilising urea and to a more limited extent acetamide and its immediate homologues as sources of nitrogen.

Writing of *Saccharomyces thermantitonum*, H. von Euler and I. Laurin[126] give particulars regarding the inverting capacity, the catalase activity, the rate of fermentation at 35°-40° C. and the growth of the species. T. Cochin and R. Sazerac[127] have observed that the maceration fluids from pressed yeast give a reddish colour with Schiff's reagent. The substances which give this reaction are not volatile, so that they cannot be identified with the lower aldehydes. Their exact nature has not been determined. E. Hägglund[128] has stated that 0·007 N sulphurous acid completely inhibits the fermentation of 1 grm. of yeast in 25 c.c. of the solution, but that 0·005 N acid does not completely inhibit its activity. The toxic effect of sulphurous acid on yeast fermentation is attributed to the undissociated acid. E Bahlcm[129] compares substances prepared from yeast with two albuminoids, metaboline and antibolin, prepared from ox pancreas, and finds they are very similar in their catalytic action on fermentation. By the action of concentrated sulphuric acid on dry yeast, a substance of acid character is obtained which accelcrates the fermentation of dextrose by yeast. A similar substance is obtained from potato skins.

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[119] *Ibid.*, 1919, **7**, No. 18, 1 ; *J.*, 1920, 244A.

[120] *J. Inst. Brew.*, 1914, **20**, 488.

[121] *Int. Cong. Appl. Chem.*, 1909 ; *J.*, 1909, 807.

[122] *Bull. Soc. Chim. Biol.*, 1914, **1**, 67 ; *J. Chem. Soc.*, 1920, i., 266.

[123] *Biochem. J.*, 1920, **14**, 483 ; *J.*, 1920, 604A.

[124] *Z. techn. Biol.*, 1919, No. 1 ; *J.*, 1920, 129A.

[125] *Ann. Inst. Pasteur*, 1919, **33**, 777 ; *J.*, 1920, 77A.

[126] *Biochem. Zeits.*, 1919, **97**, 156 ; *J.*, 1920, 77A.

Membraneless yeast cells have been obtained by R. Giaja[130] by the action of the intestinal juice of the snail, *Helix pomatia.* This juice has the property of dissolving the cell membrane of yeast, but does not decompose protein. Toluene retards the fermentative activity of these membraneless cells, as it does the normal cell, so that the effect of toluene in this respect does not depend on its action on the membrane, as previously supposed. The membraneless cells can ferment sugar similarly to the normal cells, and appear to retain their power of respiration.

Vitamines.

This important subject has been taken up very enthusiastically by various workers, and the chemical isolation of vitamines has been investigated by C. N. Myers and C. Voegtlin,[131] who have made preparations from pressed bottom yeast by autolysis and the subsequent extraction of the clear liquid with olive oil or oleic acid. The vitamine is extracted from the oil solution with weak hydrochloric acid and concentrated *in vacuo.* The preparation yields precipitates with phosphotungstic acid and with picric acid. The authors detail a method whereby much purer vitamine can be obtained by the extraction of very finely-divided dried yeast with methyl alcohol acidified with hydrochloric acid, and a subsequent complicated series of precipitations, when a final crystalline product is obtained. The important point has been brought out by the authors that polyneuritic symptoms of pigeons are readily relieved by these vitamine preparations.

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[127] *Bull. Soc. Chim. Biol.*, 1914, **1**, 75; *J. Chem. Soc.*, 1920, i., 266.

[128] *Biochem. Zeits.*, 1920, **103**, 299; *J.*, 1920, 580A.

[129] *Z. physiol. Chem.*, 1919, **106**, 133; *J. Inst. Brew.*, 1920, **26**, 168.

[130] *Comptes rend.*, 1919, **169**, 719; *J. Inst. Brew.*, 1920, **26**, 169.

[131] *J. Biol. Chem.*, 1920, **42**, 199; *J.*, 1920, 500A.

T. B. Osborne and A. J. Wakeman[132] find that in the extraction of water-soluble vitamine from yeast it is not necessary to allow the yeast to undergo autolysis. They state that such autolysis converts a large proportion of the complex nitrogenous substances of the yeast into degradation products which are extracted along with the vitamines. Fresh brewers' yeast, after washing in a centrifugal machine with ice-cold water, was added to boiling water containing 0·01% of acetic acid, and the whole boiled for five minutes and filtered. The residue was similarly treated and the two filtrates combined and concentrated. The concentrated extract was poured into 93% alcohol so that the mixture contained about 52% of alcohol by weight. The precipitate formed proved to be comparatively free from vitamine. The mother liquor was concentrated and poured into alcohol so that the final mixture was about 79%. In this way a precipitate was obtained which contained the major part of the vitamine originally present in the yeast.

R. J. Williams has already shown[133] that the "water-soluble B" fraction of yeast is necessary for the nutrition of yeast cells themselves, and now describes[134] a practical application of this knowledge to the quantitative estimation of vitamines. A sterile culture solution is prepared and the vitamine solution is added, followed by a small definite quantity of fresh pressed yeast suspension; this is incubated at 30° C. for 18 hours, the yeast filtered off, dried, and weighed. The increase of weight over that of a control solution is a measure of the vitamine present. Various precautions are given which must be observed and the author claims to get reliable results. The writers are of opinion that the use of pure culture yeast is essential in such work. Further, the carrying out of proper controls is imperative. The vitamine preparations must of necessity contain much other matter than vitamine and all influence of such should be eliminated by the use of a control in which the vitamine has been destroyed. In the writers' experience of fermentations in asparagine nutrient solutions, the addition of small amounts of various substances has been found to produce very extraordinary results. It is to be hoped that Williams will continue this important work.

BREWERY BY-PRODUCTS.

The utilisation of by-products is essential from an economic standpoint in any industry, as has been shown on many different occasions. This subject, so far as the brewing and allied industries are concerned, is still in its infancy. C. H. Field[135] gives an account of the conversion of yeast into a highly nutritious and profitable food, giving some figures regarding cost of production. The author refers to the use of brewers' yeast in place of distillers' yeast for baking purposes but does not hold out hopes of any great success in that direction. During the discussion which followed the reading of his communication, various individuals gave their experiences in trying to get bakers to use brewers' yeast, especially during the war, when conditions for transport etc. were not normal. The question of rendering the fibrous parts of spent grains and hops more digestible by the old-fashioned method of "pitting" as compared with the more modern one of drying, the author leaves as a debatable point.

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[132] *J. Biol. Chem.*, 1919, **40**, 383; *J.*, 1920, 131A.

[133] *Ann. Repts.*, 1919, **4**, 439.

[134] *J. Biol. Chem.*, 1920, **42**, 259; *J.*, 1920, 608A.

BACTERIOLOGY.

Bacteriology is a science naturally associated with the fermentation industries and its importance is being recognised more and more as time goes on. Its practical application to industry has been very ably laid down by A. C. Thaysen[136] who emphasizes its importance outside medicine.

Pitching-yeast when infected by torulæ is usually able to suppress their growth, provided of course that the infection is not too great. This is due to the fact that torulæ develop comparatively slowly in beer wort. H. Will and F. O. Landtblom,[137] however, found a torula which caused trouble in young beer. They describe the main characteristics and some of the effects of this organism, which they have designated *Mycotorula turbidans*, Will. The infection of wort and beer from brewing water has to be guarded against very carefully and a reliable method for the detection of the many organisms is one which will be of great assistance. Hitherto Hansen's method has been generally used, but R. Heuss[138] finds on making comparative tests with Hansen's and Zikes' methods[139] that the latter is more sensitive, revealing in some of the waters which he tested the presence of certain organisms which were not detected by Hansen's method.

With a view to discovering whether mould spores contain enzymes, N. and L. Kopeloff[140] prepared a spore emulsion by heating a suspension of spores to 63° C., and shaking with sand to rupture the spore wall. A 10% sucrose solution was treated under prescribed conditions with the suspension and results were obtained which

[135] *J. Inst. Brew.*, 1920, **26**, 407.
[136] *J. Inst. Brew.*, 1920, **26**, 147.
[137] *Z. ges. Brauw.*, 1919, **42**, 367; *J. Inst. Brew.*, 1920, **26**, 261.
[138] *Z. ges. Brauw.*, 1920, **43**, 177; *J.*, 1920, 607A.
[139] *Allg. Z. Bierbr. Malzfabr.*, 1915, **43**, 237.
[140] *J. Agric. Res.*, 1919, **18**, 195; *J.*, 1920, 168A.

suggest the presence of an enzyme identical with invertase. *Aspergillus niger* and *sydowi* gave the most pronounced results, while *Penicillium expansum* and *Aspergillus flavus* acted similarly but more feebly. The upper limit of concentration for the sugar solution was found to be 18–24%, using a suspension containing 100,000–400,000 spores per c.c. The formation of acid by *Mycoderma, Oidium,* and *Aspergillus niger* in media containing various carbohydrates and nitrogenous substances has been investigated by F. Boas and H. Leberle[141] who find that most of the acid is formed at the expense of the carbohydrate.[142] Where an ammonium salt of a strong acid forms the source of nitrogen the acid liberated therefrom suppresses the formation of acid from the carbohydrate and F. Boas[143] finds that under such conditions there is a production of soluble starch, from various simple carbohydrates, by *Aspergillus niger,* when a certain hydrion concentration is attained. For example if ammonium chloride as well as amino-acid is assimilated by this mould in a carbohydrate solution, the resulting liberation of hydrochloric acid promotes the formation of soluble starch and the iodine test thus affords a means of determining which form of nitrogen has been attacked. In mixtures of ammonium chloride, phosphate, and citrate with amino-acids and peptone, or with urea, the author found that it was the ammonium chloride which was attacked, and with mixtures of nitrogenous substances having different degrees of dissociation, the magnitude of the dissociation controlled the absorption into the cells of the mould, which absorption is the result of purely physico-chemical processes and is not regulated by the mould. This observation of the formation of soluble starch from simpler carbohydrates is so important that it is to be hoped that Boas' observation will be confirmed by other investigators.

J. Effront has already shown[144] that the acclimatisation of micro-organisms to toxic substances is due to an elimination of the weaker cells and survival of the fittest. Continuing this work[145] he now calls attention to the importance of employing large seeding rates to ensure a sufficiency of resistant cells.

ACETONE.

H. B. Speakman[146] has continued his studies on the production of acetone and butyl alcohol by fermentation and now details a process starting from laboratory cultures. The process is very similar to any other where pure culture fermentations are used. The name of the particular organism involved in this fermentation method is not given. The same author[147] uses "*Bacillus granulobacter pectinovorum*" for the production of acetone and butyl alcohol from starch. The starch first undergoes conversion into dextrose which passes into the cells of the organism and is there oxidised to acetic and butyric acids, the latter being reduced in part to the corresponding alcohol. Speakman[148] suggests the following scheme to represent the course of the fermentation:—

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[141] *Biochem. Zeits.*, 1918, **92**, 170; *J.*, 1920, 168A.

[142] *Cf. also* A. J. Brown, *J. Chem. Soc.*, 1886, 172, 432; 1887, 638.

[143] *Ber. Deut. Botan. Ges.*, 1919, **37**, 50; *J.*, 1920, 168A.

[144] *J. Inst. Brew.*, 1895, **1**, 91.

[145] *Comptes rend. Soc. Biol.*, 1920, **83**, 807; *Ann. Brass. et Dist.*, 1920, **18**, 363.

[146] *J. Ind. Eng. Chem.*, 1920, **12**, 581; *J.*, 1920, 555A.

$$(1)\ \underset{\text{Starch.}}{(C_6H_{10}O_5)_x} + xH_2O = \underset{\text{Dextrose.}}{xC_6H_{12}O_6}.$$

$$(2)\ C_6H_{12}O_6 = C_3H_7{\cdot}CO_2H + CH_3{\cdot}CO_2H + [O_2].$$

$$(3)\ 2C_3H_7{\cdot}CO_2H + O_2 = 2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH + 2H_2.$$

$$(4)\ CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH = CH_3{\cdot}CO{\cdot}CH_3 + H_2O.$$

$$(5)\ C_3H_7{\cdot}CO_2H + 2H_2 = CH_3(CH_2)_3OH + H_2O.$$

$$(6)\ CH_3{\cdot}CO_2H + 2H_2 = CH_3{\cdot}CH_2OH + H_2O.$$

The formation of the various substances produced in the process is satisfactorily explained by this scheme.

POWER ALCOHOL.

As was the case last year, the utilisation of various substances for the production of alcohol has been investigated. The question of using alcohol as a fuel for transport and other purposes seems to be engaging the attention of various countries, but how far it can be produced on a profitable scale still remains a subject for further enquiry. A. P. H Desborough[149] in reviewing the subject of industrial alcohol gives some figures, as far as are available at present, showing the relative cost of production in the various processes which are being tried, and also records the outline of work being carried out at the Royal Naval Cordite Factory, Holton Heath, in conjunction with the Department of Scientific and Industrial Research. A Report[150] is given of a letter to *The Times*, in which a correspondent sums up the outlook for petrol substitutes. The production of alcohol as a fuel can only be rendered a possibility when the Board of Customs and Excise are less rigid in their regulations and permit the use of other denaturants. How far the Revenue Authorities are likely to encourage progress may be fairly well gauged by the answers given in Parliament on November 4th last to various questions on the subject. Were relaxations granted there is little doubt as to future developments when one considers the demand occasioned by the high prices prevailing for petroleum oils and the comparatively limited supply of the latter, when the possible future world's consumption is taken into account,

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[147] *J. Biol. Chem.*, 1920, **41**, 319; *J.*, 1920, 381A.

[148] *J. Biol. Chem.*, 1920, **43**, 401; *J.*, 1920, 760A.

[149] *J.*, 1920, 302R.

[150] *J. Inst. Brew.*, 1920, **26**, 471.

In various countries—Straits Settlements, Holland, and Java—there is a great quantity of cassava or manioc cultivated. This has been used on the continent as a malt adjunct in brewing but a better use could be made of it in the preparation of alcohol; 30—35 gallons of 95% spirit could be obtained from a ton of the roots. Other starchy substances might be substituted for manioc for this particular purpose. The production of alcohol from calcium carbide has been tried with no small degree of success in Switzerland and this may eventually be a very strong competitor to the fermentation process. It may also be found practicable to manufacture alcohol from acetylene by way of ethylene and from ethylene from coke-oven gas.

WINES.

Prevention of the diseases of wine is of first-rate importance to the industry and the chief publications of a somewhat lean year are concerned with ways and means of freeing wines from their peculiar maladies.

The reducing action of yeast is made use of in various ways, notably as a means of overcoming certain diseases and also to eliminate detrimental flavours, odours, etc. Matthieu[151] deals with several of these factors. Oxidation products, responsible for the colour, flavour, and aroma characteristic of wines affected by the "yellow" malady, can be suppressed by re-fermentation wherein the reducing action of the yeast operates on these products. A similar treatment or even mixing with yeast will generally remove bitterness in wines. The practice of improving "flat" wine by contact with marc from the presses, depends to some extent on the reducing action of the yeast in the marc, but other factors, such as admixture with new wine contained in the marc also play a part. According to P. Carles[152] the ferric "casse" of wines cannot be entirely prevented by the presence of sulphur dioxide. The addition of citric or tartaric acid is the best treatment, the amount to be added varying with the intensity of the evil; 50 g. per hectolitre is the best quantity to add as a preliminary, and if necessary this may be increased to 150 or 200 g. in the case of certain wines. A. Piedallu, P. Malvezin, and L. Grandchamp,[153] prescribing for the same disease, pass oxygen in a finely-divided condition through the damaged wine. The gas is capable of rapidly oxidising the ferrous salts to ferric salts, which in turn are precipitated by tannins present. Wine thus clarified is not liable to further "casse." Oxygen in a suitable condition may be obtained by forcing the gas through a porcelain filter candle under pressure. H. Müller-Thurgau and A. Osterwalder[154] have investigated the maladies developed in Swiss red wines by the bacterial decomposition of tartaric acid and glycerol in some instances and of glycerol alone in others. The disease became apparent some weeks or months after the complete decomposition of the malic acid. The authors present an account of the characteristics of the maladies. From a wine in which both tartaric acid and glycerol underwent bacterial decomposition two new organisms were isolated, viz. *Bacterium tartaraphthorum* and *Bacterium tartaraphthorum* var. *a*. Both are facultative anaërobes and form non-motile and non-sporulating rods 0·8–1μ thick. Both organisms decompose tartaric acid energetically, but whilst the former also decomposes glycerol, the latter does so only to a slight extent. High acidity and high tannin content have an inhibitive influence on the maladies described, whilst high temperatures promote them. Suitable preventive measures are storage at low temperatures, use of sulphur dioxide and potassium metabisulphite, and pasteurisation, but in wines similar to those investigated these measures should not be applied until after the decomposition of the malic acid is complete.

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[151] *Bull. Assoc. Chim. Sucr.*, 1919, **37**, 174; *J.*, 1920, 309A.

[152] *Comptes rend.*, 1919, **169**, 1422; *J.*, 1920, 168A.

[153] *Ibid.*, 1920, **170**, 1129; *J.*, 1920, 463A.

[154] *Landw. Jahrb. der Schweiz*, 1919; *J.*, 1920, 345A.

P. Lindner[155] thinks that the deficiency of bouquet in wines might possibly be remedied by the use of suitable kinds of yeast for the secondary fermentation. Treatment suitable for doctoring inferior musts in order to produce marketable wines of the Moselle type is given by Wellenstein and Seiler.[156]

A. M. MacMillan and A. Tingle[157] state that the acidity of red wines and fruit juices may be determined in presence of phenolphthalein as indicator by using the spectroscope to ascertain the end-points.[158]

VINEGAR.

Oxalic acid, which is not present in normal vinegar fermentation, may be formed if over-oxidation has taken place. Commercial acetic acid may contain glyoxalic acid which, on oxidation, is converted into oxalic acid. In the latter case the quantity of oxalic produced is too small to be estimated by the usual calcium sulphate reagent, but it can be found by the calcium acetate reagent as proposed by A. Bau.[159] More reliable results are obtained using this reagent, which can be applied without previously neutralising the vinegar. For the determination of the total solids in wine vinegar, Aschoff and H. Haase[160] consider the indirect method of Lehmann and Gerum[161] gives more accurate results than a direct determination.

[155] *Woch. Brau.*, 1919, **36**, 223; *J.*, 1920, 129A.

[156] *Z. Unters. Nahr. Genussm*, 1920, **39**, 1; *J.*, 1920, 607A.

[157] *J. Ind. Eng. Chem.*, 1920, **12**, 274; *J.*, 1920, 381A.

[158] *Cf. J.*, 1918, 117T, 443A.

[159] *Chem. Zentr.*, 1920, **91**, II., 298; *J.*, 1920, 381A; also *J.*, 1918, 524A, 671A.

[160] *Z. öffentl. Chem.*, 1920, **26**, 4; *J.*, 1920, 524A.

[161] *Z. Unters. Nahr. Genussm.*, 1912, **23**, 267.

FOODS.

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The economic factor in foods is still one of great importance owing to the high prices prevailing not only in this land, but throughout the world. It has been claimed that the enforced rationing of foods during the war has had a good effect on the physique and health of the nation, but whether this is so or not, it is quite certain that in some countries rationing has resulted in malnutrition, leading to a great increase in diseases such as scurvy and rickets as well as tuberculosis, and a corresponding rise in mortality, especially amongst children.[1] Under the present circumstances, it still behoves us to examine our food carefully to make sure that not only is it sufficient in quantity but that it contains all the necessary accessory factors including vitamines, mineral salts, etc., which are essential for the maintenance of health.

The chief research work carried out during the past year to be recorded in this section has been concerned with the subject of vitamines. The isolation of one of the vitamines in crystalline form has been announced, but has not yet been confirmed. The general trend of the work seems to indicate that these substances have an important rôle to play not only in the animal but also in the vegetable kingdom, and experiments are forthcoming to show that not only animals, but also plants, as well as bacteria, require the presence of a vitamine in order to maintain the processes of growth.

The various papers which have appeared will be considered under headings as in previous reports.

Bread, Flour, etc.

Several important communications dealing with the chemistry of flour and bread-making have recently been published. Of these, reference may be made to a comprehensive and stimulating article on the laboratory control of wheat flour milling by B. R. Jacobs and O. S. Rask.[2]

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[1] M. Hindhede, *Deuts. med. Woch.*, 1919, **45**, 1236; *J. Amer. Med. Assoc.* 1920, **74**, 381; *Skand. Arch. Physiol.*, 1920, **39**, 78; *Physiol. Abst.*, 1920, **5**, 80, 134, 237.

[2] *J. Ind. Eng. Chem.*, 1920, **12**, 899; *J.*, 1920, 733A.

These chemists show that the wheat kernel may be regarded as composed of three parts, viz., the bran, the germ, and the endosperm or flour. A study of the analyses of these parts shows that each one has its own characteristic constituent. The endosperm contains at least 70% of starch, whereas this is completely absent from the bran and the germ. The bran contains a large proportion of pentosans, which are absent from the other two parts of the kernel, whilst the germ in its turn is characterised by a relatively large percentage of fat. The estimation of starch, pentosans, and fat in a sample of flour affords a ready means of calculating the approximate amounts of bran, germ, and flour present, and conversely, the analysis of a sample of wheat kernels affords information from which may be calculated, with a reasonable degree of accuracy, the amount of flour containing a definite percentage of offals (bran, germ) which can be obtained in the factory from this grade of wheat.

The question of the strength of flour in relation to its constituents is a problem that has been discussed for many years. It is generally recognised that flour containing a large proportion of gluten gives a better loaf than flour containing only a small proportion, although there are certain flours containing only a small amount of gluten which nevertheless yield excellent loaves. The tendency of late has been to attach more importance to the quality rather than to the quantity of gluten present. F. J. Martin[3] considers that certain kinds of gluten possess higher gas-retaining capacities than others, and the higher this capacity, the stronger is the flour and the better is the loaf produced. He finds that this gas-retaining power is associated with the gliadin constituent of the gluten, and indeed, there seem to be many grounds for associating the strength of flour with its gliadin content instead of with the amount of gluten which may be present. These conclusions have been confirmed by T. von Fellenberg,[4] who found that the superiority of wheat flour over rye flour and of this latter over barley flour could be correlated with the proportion of gliadin existing in each case.

W. Ostwald and H. Luers have contributed a series of papers[5] dealing with the colloidal chemistry of flour and bread, in which the value of viscosimetric measurements of suspensions of flour is particularly emphasised. The viscosity of mixtures containing as much as 20% of flour can readily be determined, even after boiling, by using large viscosimeters with large capillaries. Flours with poor baking qualities give suspensions with viscosities considerably below those given by normal flours, and inferior flours can be detected in this way. These authors also ascribe great importance to gliadin as the constituent in flour which determines its strength. The viscosity of gliadin solutions is greatly affected by changes of temperature, and the temperature at which the viscosity reaches a maximum is also the temperature at which the best bread is produced. The addition of a trace of acid, which increases the viscosity of the gliadin solution, likewise improves the quality of the bread.

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[3] *J.*, 1920, 246T, 348T.

[4] *Mitt. Lebensmittelunters. Hyg.*, 1919, **10**, 229; *J.*, 1920, 422A.

[5] *Koll. Zeits.*, 1919, **25**, 26, 82, 116, 177, 230; 1920, **26**, 66; *J.*, 1920, 499A.

The effect of the premature freezing of wheat grains on the quality of the flour which can be obtained from them has been studied by M. J. Blish.[6] It has been found that in the flour produced from frozen wheat the percentages of non-protein nitrogen, reducing sugars, and acid-reacting substances are higher than in the corresponding product from normal wheat. Apparently in the freezing process certain of the cells of the wheat are ruptured and enzymes are liberated which act on the proteins and carbohydrates with the production of smaller molecular products. Since the protein content is lowered, one would expect the strength of the flour to be reduced.

A review of the phenomena associated with ropiness in bread has recently appeared,[7] and the results are given of some interesting experiments which were designed to ascertain the cause of the contamination of wheat flour with the bacteria responsible for the production of this condition. It has been shown that wheat grown on land previously used for potatoes contains a far greater number of bacilli causing ropiness than wheat grown on ground which had previously carried some other crop. This confirms the conclusion already arrived at that ropiness in bread is due to the development in the bread after baking of one or more types of bacilli related to the potato group (*B. mesentericus*) and indicates that wheat should never succeed potatoes without the intervention of some other crop. Full directions are given in this review for cleansing a bakery which has become infected with these organisms, the spores of which are so resistant to heat that they can germinate after being kept for five hours at a temperature of 100° C.

The determination of the composition of the chemical constituents of food-stuffs has steadily progressed, especially in America, and at the same time the nutritive values of these constituents have been compared. It is recognised[8] that the proteins in wheat are not altogether satisfactory from the standpoint of nutrition and greater growth is obtained when part of the wheat is replaced in the dietary by some other grain. For example, bread containing 25% of peanut flour and 75% of wheat flour is more nutritive than bread prepared entirely from wheat flour, owing to the superior value of the proteins in peanut flour and to their being more readily assimilated in the body. Moreover, more satisfactory growth is obtained when the food contains the proteins of the entire kernels of barley, oats, rye, or wheat than when only the endosperm (flour) is employed.[9] The proteins of the cokernut press cake have also been shown[10] to have a high nutritive value.

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[6] *J. Agric. Res.*, 1920, **19**, 181 ; *J.*, 1920, 524A.

[7] J. Grant, *J.*, 1920, 283R.

[8] C. O. Johns and A. J. Finks, *J. Biol. Chem.*, 1920, **42**, 569 ; *Physiol. Abst.*, 1920, **5**, 304.

The production of good bread from flour depends not only on the flour but on the yeast employed, and many attempts have been made in the past to prepare a suitable yeast from ordinary brewer's yeast. Some of these processes are fairly complex, and it is difficult to say how a process such as the following one patented by H. W. Anderschou,[11] could be commercially adopted.

The yeast is treated successively with sodium bicarbonate, sodium salicylate, and borax solutions, followed by washing with solutions of sodium chloride and potassium carbonate. It is then aerated in the presence of nutrient salts, cane sugar, and infusion of willow, and finally mixed with cream of tartar, potato flour, and dried milk powder. After pressing, the product is ready for use. Another rather curious method for the production of leavened bread has been patented[12]; it consists in mixing the dough with lanolin as a shortening agent.

More remarkable results of a different nature have been obtained by T. C. Taylor and J. M. Nelson,[13] in the hydrolysis of certain natural starches. Maize starch, after being extracted with various fat solvents, yields on hydrolysis materials from which fats or fatty acids can be extracted. The characteristic nature of these fats has not been cleared up, but palmitic acid and an unsaturated compound of unknown constitution have been separated. If the hydrolysis is carried out by acids, the fatty material appears at the erythrodextrin stage, but it may also be produced when the hydrolytic agent is diastase or a bacillus (*B. acetoethylicum*). Compounds of fat and starch have also been prepared synthetically[14] by the treatment of ordinary fats with carbohydrates and derived substances such as mannitol. In these reactions, the glycerol is eliminated and the resulting carbohydrate-fat can be digested in the body like ordinary fat,[15] yielding an equivalent amount of energy. It will be apparent that in war time a knowledge of the way to treat fats so as to furnish the glycerol necessary for the production of explosives without rendering the remaining part of the fat molecule useless for feeding purposes would be a tremendous asset to any country.

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[9] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1920, **41**, 275; *Physiol. Abst.*, 1920, **5**, 134; *J.*, 1920, 381A.

[10] B. C. P. Jansen, *Med. geneesk. lab. Weltevreden*, 1920, 3A, 1; *Physiol. Abst.*, 1920, **5**, 360.

[11] E.P. 149,533; *J.*, 1920, 701A.

[12] H. A. Kohman, and R. Irvin, U.S.P. 1,345,680; *J.*, 1920, 637A.

[13] *J. Amer. Chem. Soc.*, 1920, **42**, 1726; *J. Chem. Soc.*, 1920, i., 660; *J.*, 1920, 668A.

[14] A. Lapworth and L. Pearson, *Biochem. J.*, 1919, **13**, 297; *J.*, 1919, 952A.

[15] W. D. Halliburton, J. C. Drummond, and R. K. Cannan, *Biochem. J.*, 1919, **13**, 301; *J.*, 1919, 952A.

Besides the proteins of cereals, the proteins of various beans have been investigated with regard to their nutritive value. Many of these beans appear to be lacking in one or other of the essential amino-acids; thus, the globulin from the Georgia velvet bean[16] (*Stizolobium Deeringianum*) contains no tryptophan, and the protein of Navy beans[17] (*Phaseolus vulg.*) no cystine. The protein of spinach leaves[18] has also been examined, whilst several methods for removing the cyanogenetic enzyme and prussic acid from Rangoon beans have been published.[19] Attention has also been called[20] to the highly nutritive soya bean, which has been the chief source of protein in the Chinese dietary for centuries and from which the most successful substitute for milk has been prepared.

Milk.

Two interesting reports[21] dealing with milk from the economic standpoint have recently been published in America. It is pointed out that milk and other dairy products are much cheaper sources of protein and energy than most materials usually included in the diet. As a source of protein, skim milk is cheaper than other foods of animal origin or than dried peas or beans, whilst with regard to heat and energy production the cost per calory in the case of milk is considerably less than in the case of meat, eggs, poultry, or fried fish. It is, therefore, a sound economic policy to encourage the breeding of cows rather than of oxen, because by means of the former, there is afforded as milk a much greater supply of proteins, fats, and carbohydrates, as well as of mineral salts and vitamines, than can be provided by the latter in the form of meat. It is stated that a quart of milk is at least as great an asset in the family dietary as a pound of meat, and from the tables which are given it is quite evident that milk is relatively inexpensive as compared with many other foods which are generally considered as affording a maximum of nutrition at a minimum price.

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[16] C. O. Johns and H. C. Waterman, *J. Biol. Chem.*, 1920, **42**, 59; *J. Chem. Soc.*, 1920, i., 515.

[17] C. O. Johns and A. J. Finks, *J. Biol. Chem.*, 1920, **41**, 379; *Physiol. Abst.*, 1920, **5**, 134.

[18] T. B. Osborne and A. J. Wakeman, *J. Biol. Chem.*, 1920, **42**, 1; *J. Chem. Soc.*, 1920, i., 516.

[19] Rothea, *Ann. Falsif.*, 1918, **11**, 361; *Physiol. Abst.*, 1920, **5**, 184; W. Koenig, *Chem.-Zeit.*, 1920, **44**, 405, 414, 433; *J.*, 1920, 525A.

[20] W. H. Adolph and P. C. Kiang, *Nat. Med. J. China*, 1920, **6**, 40; *Physiol. Abst.*, 1920, **5**, 360.

[21] *Public Health Reports by U.S. Public Health Service*, 1920, **35**, 99[illegible] *Physiol. Abst.*, 1920, **5**, 238; *Agric. Exp. Sta., Univ. of Illinois, Circular* [illegible] **235**; *Analyst*, 1920, **45**, 244.

Very little work has been published on the constitution of milk from the chemical standpoint, but some interesting papers have appeared in America concerning some of the physical constants of milk. L. L. Van Slyke and J. C. Baker,[22] find that most samples of fresh milk are slightly acid, the hydrogen-ion concentration varying from 6·50 to 7·20, with a value below 6·76 in 80% of the samples examined. Milks of low acidity (p_H above 6·80) usually contain large quantities of leucocytes, indicating a diseased condition of the udders. The acidity of milk is increased by boiling, and hence the acidity of milk may be taken as a criterion for distinguishing between normal and abnormal milks. The method of carrying out the test devised by J. C. Baker and L. L. Van Slyke,[23] is to add one drop of a saturated solution of dibromo-*o*-cresolsulphonphthalein (bromocresol-purple) in water to 3 c.c. of the milk. Normal fresh milk gives a greyish-blue colour. Boiled milk or milk heated above the usual point of pasteurisation gives a lighter colour, whilst milk from diseased udders, watered milk, skim milk, or milk containing alkaline salts gives a darker colour.

Bromocresol-purple can also be employed as a means for determining the keeping quality of milk.[24] The test is applied as above, with the modification that the pipettes and tubes employed are sterilised before use; the samples are then incubated for a given time at 18°–20° C. Milks of the best quality retain the colour unchanged for the longest period, whilst any rapid change in colour (due to the production of acidity, either through bacterial action or otherwise) denotes a relatively poor milk.

Another means of distinguishing between fresh and heated or pasteurised milk lies in the determination of the amount of carbon dioxide present.[25] Normal unheated milk never contains less than 3 to 3·5 volumes per cent. of carbon dioxide. Pasteurisation reduces this value to 2·5 or less. For the estimation of carbon dioxide, 2 c.c. only of the milk is required, and the carbon dioxide evolved is measured in the Van Slyke apparatus, using a 20% solution of lactic acid to liberate the gas. Since normal fresh milk contains about 10 volumes per cent. of carbon dioxide, this

[22] *J. Biol. Chem.*, 1919, **40**, 345; *J.*, 1920, 130A.

[23] *J. Biol. Chem.*, 1919, **40**, 357; *J.*, 1920, 130A.

[24] J. C. Baker and L. L. Van Slyke, *J. Biol. Chem.*, 1919, **40**, 373; *J.*, 1920, 130A.

[25] L. L. Van Slyke and J. C. Baker, *J. Biol. Chem.*, 1919, **40**, 335; *J.*, 1920, 130A; and L. L. Van Slyke and R. F. Keeler, *J. Biol. Chem.*, 1920 **42**, 41; *J.*, 1920, 499A.

method seems to afford a ready and accurate means of detecting heated milk.

It is well known that the poor quality of the morning milk is due to the long interval which elapses between the afternoon and the morning milkings. Now that the hours of agricultural labour are tending to become shorter, the interval between the afternoon and the morning milkings is becoming greater, and that between the morning and the afternoon milkings relatively smaller. It is not surprising to find, therefore, that there is an even greater difference at the present time[26] between the composition of morning and afternoon milk than there was before the war, although the evidence tends to show that the average composition of milk is undergoing no change.

The sterilisation of milk by electricity seems to be an excellent method for treating milk without altering its taste or its chemical properties. An apparatus for effecting the destruction of the majority of the bacteria in milk by means of an alternating current has been described by J. M. Beattie and C. F. Lewis.[27] *B. tubercolosis* and *B. coli* are completely destroyed; and as the temperature is not raised above 64° C. during the brief interval of exposure, heat cannot be the only factor responsible for the sterilisation. The effect produced is similar to that achieved by the low pasteurisation method (heating at 60°–70° C. for 30 minutes)[28] which is the best method hitherto discovered for treating milk intended for the preparation of infant's food or for cheese making, because at this temperature the enzymes are not destroyed. Sterilisation is effected more quickly by the electrical method than by pasteurisation.

Several new methods for the preparation of humanised milk have been patented. A. W. Bosworth[29] proposes to remove the fats together with the fat-soluble vitamine and the caseinogen from non-human milk, then to remove all the calcium and the phosphorus, and finally to combine the resulting serum with a portion of the fat and the caseinogen, calcium, and phosphorus so as to yield a product resembling human milk. A simpler method has been devised by H. Timpe,[30] who enriches fresh cow's milk with fat and then treats it with a mixture of sodium and potassium pyrophosphates. On heating, the indigestible portion of the caseinogen and most of the calcium salts are precipitated and are removed by means of the centrifuge, and the resulting liquid is then brought up to the required strength by the addition of lactose.

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[26] *Dairyman*, 1920, **42**, 232; *Analyst*, 1920, **45**, 138.

[27] *Special Report Series of Med. Res. Com.*, 1920, No. 49; *J.*, 1920, 292R.

[28] Orla-Jensen, *Milchw. Zentr.*, 1920, **49**, 45; *J.*, 1920, 555A.

[29] U.S.P. 1,341,040; *J.*, 1920, 525A.

[30] G.P. 319,022; *J.*, 1920, 525A.

FATS.

The most interesting point concerning fats which has appeared during the past year is that which relates to the preparation of fat on a large scale from carbohydrates by the cultivation of mould fungi. It is a matter of common knowledge that yeast cells can grow in a suitable medium with the production either of glycogen or of fat, according to the existing circumstances; and it has now been shown that by suitable treatment yeast containing as much as 50% of fat can be produced.[31] The selected yeast or fungus (*Oidium*, *Sachsia*, or *Endomyces* species) is cultivated in a liquid containing carbohydrates and nutrient salts, but of low nitrogen content. The concentration of yeast has to be maintained as low as possible, whilst exposure to the air or even aeration assists in the laying down of fat within the cells. The fat from ordinary pressed yeast contains a variety of glycerides as well as a member of the cholesterol group of substances,[32] but it is likely that the fat produced under the abnormal conditions above described may have a different composition. The possibility of producing fat (and hence of glycerol) in war-time on a large scale may be a matter of great importance.

Attention may be drawn to two communications dealing with the determination of the Polenske and Reichert-Meissl values of fats as a check on their purity. The directions given by Polenske must, as a general rule, be closely followed if accurate results are to be obtained, and V. H. Kirkham[33] points out that as the value is a function of the pressure, the value obtained in any particular case should always be corrected to normal pressure in order to give comparable results. The only detail in Polenske's directions which does not seem to be of importance is that the distillate should be cooled to 10° C. H. D. Richmond and G. F. Hall[34] find that no difference in the value is obtained when the temperature of cooling is varied between 5° and 20° C. The Reichert-Meissl value is a logarithmic function of the pressure, and variations in atmospheric pressure within ordinary limits do not affect this result.

FISH, MEAT, ETC.

Research work in relation to fish and meat has been in the direction of the discovery of methods for their preservation by freezing and other means. It has been found[35] that frozen fish kept at a temperature below zero remain palatable for several months provided they are coated with ice. Changes, however, occur, resulting in a gradual decrease in the coagulable nitrogen and a corresponding increase in ammonia and amino-nitrogen. After about two years, the fish have become uneatable. These experiments confirm the results obtained by the Food Investigation Board referred to in the last report.[36] In continuation of the work of the Board[37] an examination has been made of the bacteria present in fish, and especially in herrings, and many species have been isolated and characterised. As the result of a special study of the changes occurring in herrings under the action of bacteria, Miss Green arrived at the conclusion that preservation is effected far better by freezing the fish in brine rather than by allowing them to freeze in air. The cold brine kills many of the bacteria before they have time to spore. It was found also that ungutted herrings kept better than gutted ones.

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[31] Kriegsausschuss für pflanzliche und tierische Oele und Fette, G.P. 306,365; *J.*, 1920, 417A; G.P. 320,560; *J.*, 1920, 670A.

[32] I. S. MacLean and E. M. Thomas, *Biochem. J.*, 1920, **14**, 483.

[33] *Analyst*, 1920, **45**, 293; *J.*, 1920, 632A.

[34] *J.*, 1920, 30T.

[35] E. D. Clark and L. H. Almy, *J. Ind. Eng. Chem.*, 1920, **12**, 666; *J.*, 1920, 580A.

Experiments have also been instituted by the Food Investigation Board on the changes occurring during the storage of frozen beef and mutton. It has been found that there is no characteristic chemical difference between the tissues of beef and mutton. If they are allowed to undergo autolysis, however, marked differences in the rate and course of disintegration are observed. The main results of the investigation can be summarised in the statement that, although beef cannot be frozen satisfactorily in air, if plunged into cold brine of a certain definite strength it rapidly reaches a condition from which later on, by slow thawing, it can be obtained in a satisfactory state. The best composition of the brine has now been discovered and arrangements have been made by the Board for carrying out these processes on a commercial scale.

An investigation of the processes of putrefaction in foods has been commenced by devising means for the detection and recognition of the bacteria present in animal tissues, and further by studying the action of these bacteria on various substances. Special attention has been directed to the "black spot" disease in beef and mutton, and it has been found[38] that this is due to infection by one or more species of *Cladesporium*, a genus of world-wide distribution occurring chiefly in animals fed upon dead vegetable matter. It has now been shown conclusively that this fungus will grow and produce spores at a temperature at least five degrees below zero, whilst at 0° C., its growth is comparatively rapid. Attempts are now being made to discover the sources of infection both in New Zealand and the Argentine; it is interesting to note that the "black spot" fungus isolated from Argentine beef is identical with that from New Zealand mutton.

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[36] *Ann. Repts.*, 1919, **4**, 456.

[37] *Rept. Food Investigation Bd.*, 1919, 7.

[38] *Rept. Food Investigation Bd.*, 1919, 12.

FRUIT, VEGETABLES, ETC.

Methods for the preservation of fruit have been extensively studied by the Food Investigation Board.[39] Strawberries when picked in a ripe condition can be kept perfectly for several days at a temperature about zero, whilst if the strawberries are placed in an atmosphere maintained free from carbon dioxide by the presence of soda lime, they may be kept for three or four weeks. By lowering the temperature still more, the strawberries are obtained in a frozen condition, and in this state may be kept for several months. Unripe strawberries do not ripen in cold storage, nor after having been kept in cold storage for a day or two can the ripening process subsequently take place. Similar results have been obtained with plums, pears, and apples.

It is usual in preserving fruit in the whole condition to sterilise them by pouring boiling water upon them or heating them in one way or another. The sterilisation process may also be performed by immersing the fruit in 0·1% formaldehyde for a few hours. Strawberries treated in this way may then be preserved in sterile cold water provided all air is withdrawn by means of a pump. The colour and flavour are said to be retained better by employing this process than by any other hitherto tried. Mrs. Onslow has shown that the loss of colour in bottled fruit is due to the fact that the pigments are unstable in aqueous solution. When the fruit cells are disintegrated by the heating process, the pigments are dissolved out and subsequently undergo changes which render them colourless.

The darkening in colour which occurs in many fruits and vegetables when the tissues are injured has been shown, also by Mrs. M. W. Onslow,[40] to be due to the presence of an oxidase system composed probably of two enzymes and a substance of the nature of catechol. The actual production of colour arises from the oxidation of the catechol by air through the intermediary action of the enzyme oxygenase. In the absence of oxygen, oxygenase, or catechol, injury of the tissues is not followed by browning. It is well known that difficulty is experienced in drying fruits and vegetables owing to the discoloration which often occurs. By removing one of the components of the oxidase system this discoloration may be prevented.

In some cases, in potatoes, for example,[41] the colour produced on injury is due to the formation of melanin under the action of tyrosinase. Rapid heating of the potatoes destroys this enzyme, and they can subsequently be desiccated without any production of colour. It has also been proposed[42] to treat sliced potatoes with vegetable mucilage to protect them from air and thereby prevent the formation of the melanin. According to another patent[43] the sliced potatoes are treated with a solution containing active chlorine. On subsequently drying the potatoes, the chlorine is driven off whilst the original colour is retained.

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[39] *Rept. Food Investigation Bd.*, 1919, 17 *seq.*

[40] *Biochem. J.*, 1919, **13**, 1; 1920, **14**, 535, 541; *J.*, 1919, 434A.

[41] H. Haehn, *Z. Spiritusind.*, 1920, **43**, 90, 104, 111; *J.*, 1920, 422A.

[42] J. Carpzow, G.P. 318,980; *J.*, 1920, 465A.

The changes occurring in fruit and vegetables during growth and ripening have been the subjects of several investigations. Particular attention has been paid to the transformation during growth of the insoluble pectose into soluble pectin. The amount of pectin in various fruits increases during growth, and injury often results in the production of a greater proportion of pectin. It appears probable that pectin acts as a protective agent, especially against insect attack. Methods for the estimation of pectin by the determination of the amount of methyl alcohol which can be obtained from it have been elaborated by A. J. W. Hornby[44] and also by S. B. Schryver and C. C. Wood.[45] Pectin, of course, is the substance responsible for the setting of fruit jellies, and the proportionate amount of sugar present determines the type of jelly produced. Excess of sugar produces a soft jelly, whilst if too little is present, the jelly is tough.[46]

In connexion with the formation of syrups, reference may be made to a patent by R. Schomann,[47] who prepared a non-crystalline syrup by pressing steamed potatoes so as to obtain a juice containing 5–10% starch. The juice after evaporation was subsequently mixed with sugar to raise the amount of soluble dry substance to 66%.

Attention has been called[48] to the fact that the caramel produced by heating sugar may contain toxic furfural. Since furfural is volatile in steam it is recommended that solutions containing caramel should always be boiled before serving.

Three types of yeast have recently been described[49] which are capable of fermenting 55—66% solutions of sugar, and it is now becoming generally recognised that the 66·5% limit is too low for syrups which may be required to be preserved for any length of time.

It has been proposed[50] to utilise Jerusalem artichokes as well as potatoes for the production of alcohol on a large scale. The starch of potatoes is readily transformed into a fermentable sugar and even the process of drying slices of potato at about 40° C. suffices to bring about a considerable production of dextrose.[51]

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[43] Chem. Ges. Rhenania, G.P. 322,821 ; *J.*, 1920, 761A.

[44] *J.*, 1920, 246T.

[45] *Analyst*, 1920, **45**, 164 ; *J.*, 1920, 466A.

[46] C. H. Campbell, *J. Ind. Eng. Chem.*, 1920, **12**, 558 ; *J.*, 1920, 581A.

[47] G.P. 318,795 ; *J.*, 1920, 464A.

[48] *J.*, 1920, 288B.

[49] J. Satava, *Z. Zuckerind. Czechoslov.*, 1919, **44**, 93 ; *J.*, 1920, 420A.

[50] H. Colin, *Bull. Assoc. Chim. Sucr.*, 1919, **37**, 121 ; *Physiol. Abst.*, 1920, **5**, 257 ; M. Rüdiger, *Z. Spiritusind.*, 1920, **43**, 203 ; *J.*, 1920, 608A ; K. Windisch, *ibid.*, **43**, 292, 300 ; *J.*, 1920, 760A.

TEA, COFFEE, COCOA, ETC.

The tannin-like constituent of coffee has been investigated by K. Freudenberg[52] and found to be chlorogenic acid, which appears to be a depside of caffeic and tannic acids. Under the action of the enzyme, tannase, it breaks down giving both these acids. The author puts forward a structural formula for the substance.

The solubility of theobromine, the purine occurring in cocoa, has been determined in various solvents and a new method for estimating it in cocoas and chocolates has been devised by R. V. Wadsworth.[53] It is interesting to note that cocoa contains rather more theobromine than is stated in most textbooks, the amount being usually about 2·2% of the cocoa.

The behaviour of cocoa butter in the human organism is being investigated by J. A. Gardner and F. W. Fox.[54] So far they have found that cocoa butter is absorbed and assimilated quite readily, and even when taken in large doses does not produce any ill-effects except a slight laxative action in some subjects. It is utilised in the body to the same extent as most other fats.

Another method for estimating the amount of shell in cocoa powder has been put forward depending on the determination of the methyl groups in the pectins of the shell. Both nibs and shells, however, contain pectins, and, according to von Koers,[55] the differences are not sufficiently great to give ground on which to base a satisfactory method for the estimation of shell in cocoa powder. Reference may perhaps be made to the excellent account of modern methods of growing cocoa and of manufacturing it into its various products given in A. W. Knapp's book on "Cocoa and Chocolate."[56]

Some interesting experiments have been carried out in America on the influence of tea, coffee, cocoa, and other foods on digestion as revealed by their action on the secretion of the gastric juice. It has been shown[57] that tea and coffee, but not cocoa, quicken the heart, relax the blood-vessels, and in large quantities, cause tremors. Diuresis also occurs, being least marked after cocoa. Large quantities of sugar are found to depress the secretion of gastric juice and tend to hinder digestion. Chocolate, however, and such ingredients as milk and eggs stimulate secretion and oppose and annul the ill-effects of sugar added at the same time. The effect of the ingestion of pies, puddings, and cakes has also been investigated. It has been found that pies are digested more easily than cakes and puddings more easily than either, whilst the bad reputation of pie-crust for delaying digestion is amply justified. It is suggestive, also, that the sight of food, if prepared in an appetising manner, is found to be a more powerful stimulus than its odour, for the secretion of gastric juice.

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[51] H. Waterman and H. Holleman, *Chem. Weekblad*, 1919, **16**, 1230; *Physiol. Abst.*, 1920, **5**, 337.

[52] *Ber.*, 1920, **53B**, 232; *J. Chem. Soc.*, 1920, i., 322; *J.*, 1920, 274A.

[53] *Analyst*, 1920, **45**, 133; *J.*, 1920, 383A.

[54] *Biochem. J.*, 1919, **13**, 368.

[55] *Pharm. Weekblad*, 1920, **57**, 924; *Analyst*, 1920, **45**, 413

[56] Published by Chapman and Hall, London.

[57] P. B. Hawk and collaborators, *Amer. J. Physiol.*, 1920, **52**, 1, 28, 248. **53**, 65; *Physiol. Abst.*, 1920, **5**, 235, 302, 359.

METALLIC SUBSTANCES IN FOODS.

Attention has recently been directed to the fact that traces of most of the metals and non-metals, even the poisonous ones such as arsenic, are normally to be found in the body tissues. Zinc is one of the metals which seems to be invariably present[58] in amounts varying from 0·0009% in the case of a child to 0·005% in an old man. The amount present seems to increase with age and may be due to the retention of the zinc absorbed in the food. Apparently considerable quantities of zinc may be taken in the food without producing any toxic effects; as much as 3·24% of zinc sulphate has been found in jam[59] prepared in zinc-coated vessels.

Copper is another regular constituent of the body and indeed occurs not only in animal tissues but also in many plants,[60] particularly in the leaves. It occurs also in milk,[61] meat, egg yolk, etc., and probably exerts no injurious action, provided the amount is below a certain limit.

Another metallic poison liable to be present in food is lead, especially where food has come into contact with a lead glaze.[62] In this connexion attention may be drawn to the fact that, in America, lactic acid is frequently used instead of citric and tartaric acids in the manufacture of mineral waters. Some preparations of this substance, however, have been found to contain considerable quantities of lead, and care should therefore be exercised in testing this substance prior to use. Lead and arsenic also occur frequently in cream of tartar, although English makers are usually on the lookout to prevent contamination with these poisons.

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[58] S. Giaya, *Comptes. rend.*, 1920, **170**, 906; *J. Chem. Soc.*, 1920, i., 458.

[59] E. Salkowski, *Z. Unters. Nahr. Genussm.*, 1916, **33**, 1.

[60] E. Rost, *Die Umschau*, 1920, **24**, 201; *Physiol. Abst.*, 1920, **5**, 271.

[61] E. Fleurent and L. Levi, *Bull. Soc. Chim.*, 1920, **27**, 440; *J. Chem. Soc.*, 1920, i., 584.

[62] H. Masters, *Lancet*, 1920, i., 1394; *Physiol. Abst.*, 1920, **5**, 253.

CATTLE FOODS.

Various methods[63] have been patented during the past few years for producing cattle foods from wood and other cellulosic materials. Generally the process consists of treatment with an alkali followed by an oxidising agent such as chlorine or sodium peroxide or potassium nitrate, oxygen carriers such as iron or manganese salts being employed. Maize cobs[64] have also been used and the treatment in this case consists of digestion with weak sulphuric acid, which hydrolyses a portion of the cellulose to sugars. Processes have also been patented[65] for treating oil cakes and the like with the object of converting them into materials fit for human food. As the processes are dependent on the use of strong alcohol, they are not likely to be adopted in this country.

A rather ingenious method for improving straw fodder has been proposed by H. Pringsheim and S. Lichtenstein.[66] A solution of ammonium chloride, kainite, and sodium phosphate is poured over the straw which is then inoculated with a non-pathogenic *Aspergillus* species. Growth of the mould rapidly takes place with evolution of heat so that the fodder has to be turned over from time to time. As much as 8% of protein has been obtained in the fodder by this means. Various other nitrogenous substances could probably be used in the nutrient fluid, including urea, which it is known[67] can be converted fairly rapidly by bacteria into protein.

VITAMINES.

The search for vitamines in all kinds of foodstuffs and other materials still continues with unabated ardour, and from the results published during the past year[68] we can form a rough idea of the distribution of the various vitamines in nature. Although some authors have reported the discovery of new vitamines, there does not seem sufficient evidence yet to warrant the admission of the existence of more than the three previously recognised, which, in partial accordance with a suggestion of J. C. Drummond,[69] we shall designate vitamines A, B, and C, respectively, and understand by vitamine A what has been termed previously the "fat-soluble vitamine" which has been shown to be one of the chief factors in the causation of rickets; vitamine B, the "antineuritic or water-soluble vitamine," and vitamine C, the "antiscorbutic vitamine." Not only have the various vitamines been detected in the common foodstuffs, but attempts have been made in certain quarters to obtain quantitative data showing the actual amounts of particular foods which are required to supply a sufficient amount of a vitamine to maintain the health of an animal.

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[63] F. Lehmann, G.P. 307,616; *J.*, 1920, 423A. P. Strahl, G.P. 317,111; *J.*, 1920, 423A. H. Mühlenbein, G.P. 305,090; *J.*, 1920, 346A.

[64] F. Scurti and G. Morbelli, *Staz. Sper. Agrar. Ital.*, 1919, **52**, 238; *J.*, 1920, 464A.

[65] K. Erslev, E.P. 128,216; *J.*, 1920, 423A. Holstein Oelwerke, G.P. 318,413; *J.*, 1920, 423A.

[66] *Cellulosechemie, Beiblatt to Papierfabr.*, 1920, **1**, 29; *J.*, 1920, 733A.

[67] W. Voltz, *Biochem. Zeits.*, 1920, **102**, 151; *J.*, 1920, 556A.

[68] *Report on Vitamines by the Medical Research Committee*, 1919.

[69] *Biochem. J.*, 1920, **14**, 660; *J.*, 1920.

Perhaps the most important advance during the year has been achieved by R. J. Williams,[70] whose work on the vitamine requirements of yeast has led him to put forward a method for estimating the vitamines in various foods by ascertaining their effect on the rate of growth of yeast cells.

The growth of other vegetable organisms has also been found to be dependent on the presence of traces of other substances of the nature of vitamines. The brown rot organism of peaches and plums, *Sclerotinia cinerea* (Bon.) *Schroter*, does not grow in ordinary nutrient solutions until a small amount of peach, prune, or apple juice is also added.[71] The stimulating substance (? vitamine) can be adsorbed by fuller's earth from the fruit juice, and the powder with adsorbed vitamine, on being added to a nutrient solution containing the organism, again exerts its stimulating influence. According to R. Legroux and J. Mesnard,[72] bacteria also require a vitamine to promote normal growth. When a filtered extract of red blood corpuscles made at 80° C. with dilute saline solution is added to a nutrient medium inoculated with the influenza bacillus, the propagation of the latter is greatly stimulated. The extract especially seems to prolong the time of active growth. It seems possible then that vitamines have an important rôle to play, not only in the animal but also in the vegetable kingdom, and in confirmation it has been noted by F. A. Mockeridge[73] that the stimulating influence of manure on the growth of certain plants can be traced to the action of certain substances which are of the nature of vitamines.

The manner in which these vitamines exert their action in the body is still veiled in mystery. It is not known whether they are required for the building up of a particular vital tissue or whether they act as stimulants of certain glands. The different vitamines have doubtless different functions to perform and are concerned with different organs in the body. The study of the histological structure of the tissues of de-vitaminised animals may be expected to afford information on this point, and already

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[70] *J. Biol. Chem.*, 1919, **38**, 465; 1920, **42**, 259; *J.*, 1919, 692A; 1920, 608A.

[71] J. J. Willaman, *J. Amer. Chem. Soc.*, 1920, **42**, 549; J. *Chem. Soc.*, 1920, i., 411.

[72] *Comptes rend.*, 1920, **170**, 901; *Physiol. Abst.*, 1920, **5**, 379.

[73] *Biochem. J.*, 1920, **14**, 432; *J.*, 1920, 606A.

W. Cramer[74] has called attention to a glandular type of adipose tissue present in all types of mammals, and described usually as brown fat, which is peculiarly affected by vitamines. He points out that this tissue is quite distinct from ordinary adipose tissue, and retains its lipoids under conditions which cause the disappearance of ordinary fatty tissue. When vitamines are completely withheld the lipoids disappear from this tissue and also from the adrenal cortex which appears to be closely related to it. The gland itself persists, however, and when vitamines are restored it returns to its former condition. He suggests that the functional activity of this tissue is concerned in the prevention of the deficiency diseases.

Other changes have also been noted in animals suffering from want of vitamines. After the withdrawal of vitamine B, for instance, the most noticeable changes[75] are complete atrophy of the thymus and hypertrophy of the adrenals, whilst other pathological disturbances are referred to below in discussing the function of vitamine C.

Vitamine A.—This vitamine has been found to be more widely distributed than was formerly thought to be the case. Besides butter, dried tomato,[76] clover, lettuce, carrot, lucerne, spinach, and other vegetables have been found to contain large quantities of vitamine A. What is perhaps more important to the margarine manufacturer is that some of the vegetable oils, for example, palm oil,[77] possess considerable quantities of this vitamine. Nuts such as brazil, barcelona, pea, walnuts, almonds, and butter nuts contain only very small amounts of the vitamine, if any.[78]

The question of the relative thermo-stability of this vitamine has been discussed, and agreement has not yet been reached. On the one hand[79] J. C. Drummond has stated that it is readily destroyed by heat, whilst on the other hand H. Steenbock and P. W. Boutwell[80] find that even at a temperature considerably above the boiling point no appreciable destruction takes place. It must be pointed out, however, that in the one case the vitamine was contained in butter or other fatty material, whilst in the other it was present in a natural state in vegetable cells. Possibly it exists in the cells in a combined state and is thus able to resist the action of heat.

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[74] *Brit. J. Exper. Pathol.*, 1920, **1**, 184; *Physiol. Abst.*, 1920, **5**, 317.

[75] A. D. Emmett and F. P. Allen, *J. Biol. Chem.*, 1920, **41**, liii.; *Physiol. Abst.*, 1920, **5**, 240.

[76] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1920, **41**, 549; *J.*, 1920, 422A.

[77] J. C. Drummond and K. H. Coward, *Biochem. J.*, 1920, **14**, 668; *J.*, 1920, 798A.

[78] K. H. Coward and J. C. Drummond, *Biochem. J.*, 1920, **14**, 665; *J.*, 1920, 798A.

[79] *Biochem J.*, 1919, **13**, 81, 95; *J.*, 1919, 435A.

[80] *J. Biol. Chem.*, 1920, **41**, 163; *J.*, 1920, 277A.

An interesting theory has also been put forward,[81] according to which vitamine A is to be regarded as one of the vegetable pigments. In many cases yellow oils and green vegetables have been found to contain vitamine A, but as many colourless oils[82] and fats, such as dog fat,[83] contain large amounts of this vitamine, it is difficult to reconcile these facts with the theory, unless the existence of a "leuco" form[84] of the pigment can be substantiated. Moreover, O. Rosenheim and J. C. Drummond[85] have shown that the chief vegetable pigments, carrotene and xanthophyll, cannot replace vitamine A in the diet.

Contrary to previous conclusions, it has been reported[86] that both lard and cottonseed oil contain appreciable amounts of vitamine A, but it is doubtful whether the growth-effects observed were not due to faulty preparation of the basal diets. J. C. Drummond and K. H. Coward[87] have, however, noted the occurrence of the vitamine in fresh, unrefined pig fat, so that it is possible that the occurrence of the vitamine in lard may be dependent on the kind and extent of refining to which it has been subjected.

With the ultimate aim of isolating the pure vitamine, several authors[88] have investigated the extractability of the substance by various solvents. It is soluble in alcohol, and the alcoholic extract, after removal of the alcohol, still retains its active properties. Even the ethereal extract of this residue possesses highly active properties. The final material obtained by extraction of vegetable tissues in this way is of an oily nature, but it is undecided whether the fat-soluble vitamine is itself a fat. It resists hydrolysis with cold alcoholic potassium hydroxide, and can be recovered in the carrotene fraction of the unsaponifiable matter[89]; the probability is that the vitamine is not a true fat.

A deficiency of the fat-soluble vitamine in the diet shows itself in various ways in the animal body. One of the usual symptoms

[81] H. Steenbock and collaborators, *J. Biol. Chem.*, 1920, **41**, 81, 149; *J.*, 1920, 245A, 277A.

[82] L. S. Palmer, *Science*, 1919, **50**, 1; *Physiol. Abst.*, 1920, **5**, 92.

[83] J. C. Drummond and K. H. Coward, *Biochem. J.*, 1920, **14**, 668; *J.*, 1920, 798A.

[84] H. Steenbock, *Science*, 1919, **50**, 352; *Physiol Abst.*, 1919, **4**, 492.

[85] *Lancet*, 1920, i., 862; *Physiol. Abst.*, 1920, **5**, 135.

[86] A. L. Daniels and R. Loughlin, *J. Biol. Chem.*, 1920, **42**, 359; *J.*, 1920, 609A.

[87] *Biochem. J.*, 1920, **14**, 668; *J.*, 1920, 798A.

[88] S. S. Zilva, *Biochem. J.*, 1920, **14**, 494; *J.*, 1920, 609A. H. Steenbock and P. W. Boutwell, *J. Biol. Chem.*, 1920, **42**, 131; *J.*, 1920, 500A.

[89] S. S. Zilva, *Biochem. J.*, 1920, **14**, 494; *J.*, 1920, 609A. H. Steenbock and P. W. Boutwell, *J. Biol. Chem.*, 1920, **42**, 131; *J.*, 1920, 500A.

is a peculiar disease of the eyes termed keratomalacia or xerophthalmia, which has been observed in rats, rabbits,[90] and other animals, besides children, after the withdrawal of the fat-soluble factor. As it does not always occur, and, moreover, does not seem to be attributable to any specific bacillus, this disease appears to be due more likely to a lessening of the resistance of the corneal tissue to bacterial attack rather than to actual degeneration of this tissue through lack of the vitamine.[91] In a somewhat similar way it has been shown undoubtedly that lack of vitamine A predisposes to rickets,[92] but other factors are also involved, although probably deficiency of vitamine A may be regarded as the predominant factor in the etiology of the disease.

Vitamine B.—The distribution of this vitamine is gradually becoming better known. It has been shown [93] to be present in the edible parts of the orange, lemon, and grape-fruit, the juices of which are about equivalent in antineuritic power to cow's milk. The juices may be brought to a state of dryness by desiccation on starch without losing their activity. Apples, pears, and prunes, besides tomatoes, spinach, carrots, turnips, and cabbage, contain the vitamine, whilst lucerne and clover appear to be exceptionally rich in it. In cereals vitamine B has been shown to be concentrated in the germ and outer layers of the grain, but in the potato [94] the vitamine is distributed throughout its substance, and is not confined entirely to the outer layers. It can be extracted [95] from rice bran by 0·3% hydrochloric acid, 70% alcohol, or 96% alcohol containing hydrochloric acid, and the extracts when dried on washed white rice are found to have about equal activities in preventing polyneuritis in pigeons. A method of extraction with dilute mineral acids has been patented by R. Bosshard and F. Hefti.[96]

In the method of estimation proposed by R. J. Williams, referred to above,[97] the growth of yeast in a nutrient solution under the action of the vitamine is determined by finding the increase in the weight of the yeast or in the number of the cells in a given time and this is compared with the corresponding growth in the absence of the itamine. The experiments seem to show that yeast cells cannot ultiply unless this vitamine is present, although other authors[98] ave suggested that the responsible agent concerned is not necesarily identical with vitamine B. It is well known that yeast rowth is affected by traces of many substances; indeed, Williams imself notes that asparaginic acid behaves somewhat similarly the vitamine. Moreover, Lumière[99] states that vitamine extracts hich have been heated to 135° C. and have thereby lost their ower to cure polyneuritis in pigeons, nevertheless still exert their timulating action on the growth of yeast cells, and he draws the ference that the vitamines, as ordinarily characterised, are not ssential for the adequate nutrition of these organisms. The evelopment of this work will be watched with great interest ecause if it should be shown that the accelerated growth of yeast actually due to vitamine B, this method of detecting and estiating the vitamine in the course of a few hours will be a great dvance on the present biological method, which requires weeks r even months.

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[90] V. E. Nelson and A. R. Lamb, *Amer. J. Physiol.*, 1920, **51**, 530; *Physiol. Abst.*, 1920, **5**, 185.

[91] M. Stephenson and A. B. Clark, *Biochem. J.*, 1920, **14**, 402.

[92] E. V. McCollum, N. Simmonds, and H. T. Parsons, *J. Biol. Chem.*, 1920, **41**, xxxi.; *Physiol. Abst.*, 1920, **5**, 241.

[93] T. B. Osborne, L. B. Mendel, and A. J. Wakeman, *J. Biol. Chem.*, 1920, **42**, 465; *J.*, 1920, 609A.

[94] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1920, **41**, 451; *Physiol. Abst.*, 1920, **5**, 135.

[95] B. C. P. Jansen, *Med. Geneesk. Lab. te Weltevreden*, **3**A, 22; *Physiol. Abst.*, 1920, **5**, 361.

[96] G.P. 320,785; *J.*, 1920, 675A.

[97] *J. Biol. Chem.*, 1919, **38**, 465; 1920, **42**, 259; *J.*, 1919, 692A; 1920, 608A.

The isolation of the pure vitamine has been announced by F. Iofmeister[100] and also by C. N. Myers and C. Voegtlin.[101] The ormer extracted it from rice flour and the latter from dried east. Although showing active antineuritic properties when first repared, it is stated to lose its activity rapidly on keeping. Iofmeister has analysed it, given it the formula $C_5H_{11}NO_2,HCl$, nd christened it oridine hydrochloride. However, this is not the irst time a crystalline vitamine has been stated to have been repared,[102] and further particulars must be awaited before it can e regarded as an established fact.

Vitamine C.—The principal sources of this vitamine are green egetables such as cabbage, also swedes and orange and lemon uices. The potato[103] also contains vitamine C and boiling in vater for fifteen minutes does not destroy it. By adopting certain recautions, potatoes baked at 200° C. for a short time and then ried at a low temperature may yield a product with definite anticorbutic properties. Extracts of raw beef[104] do not seem to contain itamine C.

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[98] A. D. Emmett and collaborators, *J. Biol. Chem.*, 1920, **43**, 265, 287; ., 1920, 671A.

[99] A. Lumière, *Comptes rend.*, 1920, **171**, 271; *J. Chem. Soc.*, 1920, i., 652.

[100] F. Hofmeister, *Biochem. Zeits.*, 1920, **103**, 218; *J.*, 1920, 581A.

[101] *J. Biol. Chem.*, 1920, **42**, 199; *J.*, 1920, 500A.

[102] See R. R. Williams and Seidell, *Ann. Repts.*, 1918, **3**, 410.

[103] M. H. Givens and H. B. McClugage, *J. Biol. Chem.*, 1920, **42**, 491; ., 1920, 609A.

[104] R. A. Dutcher, E. M. Pierson, and A. Biester, *J. Biol. Chem.*, 1920, **42**, 01; *J.*, 1920, 609A.

The vitamine does not appear to be quite so susceptible to heat[105] as was formerly supposed. Orange juice especially can be heated to a temperature as high as 130° C. without losing its activity. The resistance of the vitamine to destruction by heat is increased when the heating takes place in an atmosphere free from oxygen, and it is suggested that the conditions of canning of fruits and vegetables might be so adjusted as to lead to a retention of the active vitamine in the canned product.

It is possible by simple evaporation of orange juice to obtain a fairly active syrup which can cure scurvy in animals.[106] A better method of preparing the vitamine in a concentrated form and one which promises to be of considerable commercial importance is that discovered by M. H. Givens and H. B. McClugage.[107] Orange juice is mixed with corn syrup and forced as a fine spray into a chamber where it meets a current of air heated to 75°-80° C. It is converted into a dry powder almost instantaneously and the product protects guinea-pigs completely from scurvy. The dried vitamine retains its antiscorbutic properties for several months. The process of manufacture is, of course, similar to the Merrell-Soule patent process for making milk powder.

The importance of this vitamine in daily life can be illustrated by reference to R. H. A. Plimmer's case[108] of four young pigs which had been fed for some time entirely on cooked food, a mash composed of meal, sharps, and turnips. The symptoms suggesting scurvy were bent limbs, swollen joints, loss of appetite, and general stoppage of growth, and on being touched the animals squealed with great frenzy. On giving the same food as before to the pigs, but uncooked, improvement rapidly set in. In from two to five weeks the limbs straightened out, the appetite increased and growth set in once more, and on being handled they squealed no more than is customary with pigs. The pigs were locally said to be suffering from rheumatism, or rickets, or "pig gout," but it is quite evident that they were really suffering from lack of vitamine C.

Other instances where the lack of green vegetables, accompanied by the practice of thoroughly cooking all the food (and thus destroying the vitamines), has resulted in the outbreak of scurvy[109] or in the production of minor troubles, such as decaying teeth etc.,[110] could be given, but reference can only be made to a question of great interest raised by Steenbock[111] and others, who show that the milk of cows kept on grains, roots, and no fresh green vegetables gradually loses its antiscorbutic properties. On turning the cows out to grass the antiscorbutic property of the milk quickly returns. It appears quite likely that nowadays winter milk is not so nourishishing from this point of view as summer milk, and steps should be taken, by attention to diet, to remedy this undesirable condition.

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[105] E. M. Delf, *Biochem. J.*, 1920, **14**, 211 ; *J.*, 1920, 422A.

[106] A. Harden and R. Robison, *Biochem. J.*, 1920, **14**, 171 ; *Physiol. Abst.*, 1920, **5**, 187 ; *J.*, 1920, 422A.

[107] *Amer. J. Diseases of Children*, 1919, **18**, 30 ; *Physiol. Abst.*, 1919, **4**, 455.

[108] *Biochem J.*, 1920, **14**, 570.

[109] H. Chick and E. J. Dalzell, *Brit. Med. J.*, 1920, ii., 546 ; *Physiol. Abst.* 1920, 5, 418.

[110] P. R. Howe, *Dental Cosmos*, 1920, **62**, 586, 921 ; *Physiol. Abst.*, 1920, **5**, 307, 418.

PELLAGRA.

The results of the following two investigations confirm the view that this disease is due to the lack of an element in the food, which may be a vitamine, an essential amino-acid, or some other substance or group of substances.

The first experiment was carried out by J. Goldberger and G. A. Wheeler[112] in which a number of healthy adult male convicts were kept on a low protein diet resembling that usually found in pellagra-producing districts. The experimental period lasted for 6½ months and during this time six of the subjects developed the disease. The remaining convicts of the camp, numbering 108, were exposed to the risk of infections of various kinds, but no case of pellagra occurred. It seems evident, therefore, that the cause of this disease is to be found in deficient food of some kind, the exact nature of which, however, has yet to be determined.

A condition closely resembling pellagra has been produced by H. Chick and E. M. Hume[113] in monkeys by feeding them on a diet containing ample vitamines but deficient in protein. Subsequent addition of tryptophan, lysin, arginine, or histidine did not lead to recovery, but after caseinogen a temporary gain in weight occurred, which, however, was not maintained. The exact cause of this disease still remains unknown.

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[111] E. B. Hart, H. Steenbock, and N. R. Ellis, *J. Biol. Chem.*, 1920, **42**, 383; *Physiol. Abst.*, 1920, **5**, 307.

[112] *J. Trop. Med. Hyg.*, 1920, 23, 207.

[113] *Biochem. J.*, 1920, **14**, 135.

SANITATION AND WATER PURIFICATION.

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The progress which has been made during the year under review still bears the impress of war conditions, and indications are everywhere evident that the resulting economic strain, in labour conditions, increased cost of materials, and shortage of money, has had a retarding influence. Nevertheless, it is to be hoped and expected that this influence will be only temporary, and that the seeds of progress sown during the year will yield a rich harvest in the time to come.

SANITATION.

Under this heading it is proposed to refer to the treatment of sewage and liquid trade refuse, the prevention of river pollution, the disposal of towns' solid refuse, and disinfectants.

Sewage.

During the war sewage disposal works, more especially those where the effluent was not discharged into streams which served as sources of water supply, did not receive the attention of pre-war days, with the result that plant was necessarily allowed to deteriorate and new schemes, and schemes of extension to existing works, were held up. Since the war a certain amount of lee-way has been made up, but there is still a considerable reluctance on the part of the larger Local Authorities to embark upon the large schemes which are necessary to purify their sewage properly. The smaller Local Authorities have not been so backward, and in many cases have seized the opportunity afforded by the break-up and sale of large estates to purchase the freehold of the sites of their sewage disposal works which they formerly rented.

As during the previous year, much interest has centred in the experiments being carried out with the "activated sludge" or "bio-aeration" method of sewage purification. E. Ardern[1] has given the results of the continued operation of the plant installed in October, 1917, at the Withington Sewage Works of the Manchester Corporation. Some further details are contained in the Annual Report of the Rivers Department of the Corporation for the year ending March 31st, 1920.[2] These Reports are awaited year by year with much interest, as they invariably make considerable additions to our knowledge of the subjects with which they deal. The Withington plant depends upon the blowing of air through a mixture of sewage and activated sludge. It is worked on the continuous flow principle, and with a capacity of 55,000 gallons in the aeration chamber and 27,000 gallons in the settlement tank, an average daily volume of 263,000 gallons of sewage has been treated. In times of wet weather as much as 500,000 gallons has been treated in one day. The results obtained have demonstrated the possibility of producing a satisfactory effluent by the process when dealing with a uniform flow of sewage and with an increased flow of diluted sewage in wet weather, but unfortunately it has not been possible to attempt to deal with the actual variations in flow which occur in times of storm. The initial cost of the installation was £2174, but details of the working cost are not yet available.

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[1] *J.*, 1920; 60T; *Surveyor*, Dec. 24, 1920, 427.

At the Davyhulme Works of the Manchester Corporation a unit continuous-flow plant, designed to treat a million gallons of sewage per day, has been constructed and commenced operations during the last few days of the year under review. This plant was designed after full consideration of the latest information with regard to the construction of aeration tank, diffuser tiles, and baffle walls, and the results of its working will be awaited with much interest. It should be mentioned that Activated Sludge, Ltd., in consultation with Dr. Ardern, are responsible for the equipment of the plant, which is designed to give a spiral movement to the sewage as it passes through the aeration tank.

At. Birmingham J. D. Watson has constructed, for the Birmingham, Tame, and Rea District Drainage Board, three unit experimental plants, with a view to obtaining information as to the comparative cost of treating sewage (A) on the fill and draw method by air-blowing of activated sludge, (B) on the fill and draw method by agitation of activated sludge, and (C) by means of percolating filters. Each unit is designed to deal with 30,000 gallons per day but the experiments have not yet commenced.

W. H. Makepeace[3] has reported upon the results of sixteen months' experiments conducted at the Tunstall Sewage Works of the Stoke-on-Trent Corporation. At these works, although the sewage is very strong, it contains a large amount of pottery works' refuse (slip) which readily settles, and in settling carries down some

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[2] *Surveyor*, Dec. 3, 1920, 375.

[3] *Report to Sewage Department, Stoke-on-Trent*, April, 1920.

50% of the organic matter contained in the sewage. This preliminary settlement yields a tank effluent which still has an average oxygen absorbed figure of 7·0 parts per 100,000, and it is with this liquid that the experiments have been conducted. Air was blown into the mixture of sewage and activated sludge through diffusers, and a continuous flow through the aeration tank was maintained at an average rate of 120,000 gallons per day. Variations in the flow during wet weather were also dealt with up to a maximum of four times the average dry weather flow. An effluent of a high degree of purity has been consistently obtained and the sludge contains 4·5% of nitrogen calculated on the dry solids. Based upon these experiments an estimate has been prepared for a scheme, partly employing activated sludge and partly bacterial filters, to deal with the sewage of a population of 50,000. The capital cost is £85,000 and the annual working cost £4372, as compared with £125,000 and £6800 respectively for a scheme wholly on well-known artificial biological lines.

At Sheffield, J. Haworth has completed the construction of the million-gallon unit to which reference was made in last year's Report, and operations were commenced in November. Mr. Haworth relies for aeration of the sludge and sewage upon an ever-changing surface exposed to the atmosphere by means of paddles, and the process attempts to accelerate similar processes to those which occur in the bed and throughout the body of the water during the self-purification of rapidly flowing streams. The sewage passes along channels rather than through a tank. At the end of the year the process of building up a sufficient quantity of activated sludge had not been completed, so that the whole of the sludge leaving the aeration channels was being returned to them with the inflowing sewage, but the plant was dealing with the whole of the flow of sewage from the Tinsley district up to three times the daily dry weather flow. The average daily volume treated was about a third of a million gallons and the effluent could be considered very satisfactory. The publication of the results of the further operation of the plant will be of great interest, as the results already obtained warrant the assumption that a considerable saving in the construction of further sewage purification works can be effected by the adoption of the activated sludge process at Sheffield.

At several other places in this country experiments have been conducted on the new process, but in no case, except perhaps with the weak Worcester sewage, on as large a scale as at the places above mentioned. In America large-scale experiments have been continued at Milwaukee by T. C. Hatton,[4] and the construction of a large plant to deal with 65,000,000 gallons of sewage per day has been commenced. Hatton favours the arrangement of the diffusers transverse to the flow of the sewage, and considers that the spiral motion which is aimed at in the Davyhulme plant is liable to allow a central core of unpurified sewage to pass along. Equally favourable reports upon the process are to hand from Houston (Texas), Cleveland (Ohio), Worcester (Mass.), Champaign, Urbana (I l.),[5] and Folsom (Cal.).[6] At the latter place the sewage of a population of 1500 has been treated for over two years with excellent results, although the plant has been operated by convict labour, which is notoriously unreliable.

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[4] *Eng. News Rec.*, May 20, 1920, 990; *Surveyor*, July 9 and 16, 1920, 21, 48

Experiments at Sydney have been described by J. M. Smail.[7] They have been on a large scale, two fillings a day, and sewage has been treated at the rate of nearly a million gallons per day. At Shanghai experiments are about to commence, according to a communication from C. H. Godfrey, Commissioner of Public Works.

It will thus be seen, from the by no means exhaustive list of places mentioned above, that much experimental work has been done, and, broadly speaking, it may be said that the process has justified itself for the production of a satisfactory effluent in all cases where the sewage has not been exceptional in character, and where the variations in the rate of flow have not been large. It must be conceded, judging from printed reports and from conversations with actual workers in Canada and America, that the experimental work has been tackled across the Atlantic on a far larger scale than in this country, but the criticism may be offered that these experiments have not been used for the elucidation of the scientific problems of the process as much as they might and should have been, for after all it is only when the mechanism of the process is thoroughly understood that the best conditions for carrying it out can be formulated.

With regard to the scientific work which has been carried out on the activated sludge process during the year, reference should be made to the work of H. M. Wilson and J. W. H. Johnson,[8] who have investigated the effect of acid and alkaline effluents and of other trade effluents likely to occur in sewage. Their results indicate a certain adaptability of the organisms of the sludge to deal with these substances, and they state that whether an acid or an alkaline sewage is used there is a tendency to produce a neutral effluent. The Development Commissioners[9] refer to the work of G. J. Fowler and E. Ardern and to the experiments at the Rothamsted Experimental Station by E. H. Richards and G. C. Sawyer. Further details of these experiments are expected to be published shortly, but some remarkable results showing the effect of varying periods of aeration upon the production of sludge and its nitrogen content are of interest. Contributions by P. Courmont and A. Rochaix,[10] F. Diénert,[11] R. Cambier,[12] and L. Cavel,[13] have been directed towards bacterial examinations of the sludge and effluents and the fermentative properties of the sludge, as well as to studies of the rate of disappearance of ammonia and the rate of nitrification. Chloroforming the sludge does not materially affect the coagulation of colloidal matter, but nitrification is prevented. The question as to whether atmospheric nitrogen is fixed by activated sludge still remains unanswered, although G. J. Fowler[14] cites experiments which indicate but do not prove the possibility of such a fixation.

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[5] *Eng. News Rec.*, May 20, 1920, 1034.

[6] *Eng. News Rec.*, June 24, 1920, 1260.

[7] *Municipal and County Engineer*, Sept. 25, 1920, 119; *Thirty-first Report of the Metropolitan Board of Water Supply and Sewerage*, Sydney, 1920.

[8] *Report to West Riding Rivers Board.*

[9] *Tenth Report of the Development Commissioners*, 1920. (H.M. Stationery Office.)

With regard to the utilisation of activated sludge as a manure the difficulty of drying still stands in the way. In spite of the adverse reports of the Royal Commission on Sewage Disposal as to the manurial value of ordinary sewage sludge, there are many instances of such sludge being used with distinctly beneficial results, and in view of the world shortage of organic manures it would seem that further efforts should be made to render such sludge available. The few instances in which efforts have been made to degrease, dry, and sterilise the sludge have met with success, and there is an undoubted field for the use of dry powdered sludge as a fertiliser base and to prevent " cementation " of artificial compound manures. With activated sludge the problem is more difficult, as the sludge does not contain as much grease as ordinary sewage sludge, and preliminary experiments in this country to de-water the sludge by pressing, centrifugal action, or electrical treatment, down to a point at which drying by means of heat becomes commercially possible, have not yet proved a success. Some experiments by J. Haworth at Sheffield on the use of a suction drier are more promising. There are indications that the activated sludge produced at different towns is very variable in character, and T. C. Hatton states that the activated sludge at Milwaukee can be acidified and de-watered by pressing, and that the whole operation of de-watering and drying the sludge, though expensive, can be accomplished at such a cost as to permit of the sale of the dried product at a slight profit. He is at present investigating the possibility of using centrifugal machines for the preliminary de-watering of the Milwaukee activated sludge.

The manurial value of activated sludge has been investigated at

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[10] *Comptes rend.*, 1920, **170**, 75, 967 ; *J.*, 1920, 171A, 423A.

[11] *Ibid.*, **170**, 762, 899, 1089, 1134 ; *J.*, 1920, 347A, 382A, 424A.

[12] *Ibid.*, **170**, 681, 1417 ; **171**, 57 ; *J.*, 1920, 347A, 525A, 556A.

[13] *Ibid.*, **171**, 1406 ; *J.*, 1921, 96A.

[14] *J. Indian Inst. Sci.*, 1920, **3**, 256.

Withington by E. Ardern,[15] and at Rothamsted by W. E. Brenchley and E. H. Richards,[16] with very favourable results. They conclude that the nitrogen in the sludge is more available for plant life than the nitrogen in ordinary sewage sludge, and E. J. Russell estimates the present-day value of the sludge as approximately £1 per ton for each 1% of nitrogen. This valuation does not perhaps allow sufficiently for the humus constituents of the sludge. Experiments upon the possible enhancement of the manurial value of the sludge by degreasing and sterilisation have not been carried out. If it should be proved that the high nitrogen content of activated sludge is due to its abnormally high content of higher organisms, the well-known experiments at Rothamsted on soil sterilisation suggest that probably a partial sterilisation would be of more value than complete sterilisation.

In recent years much attention has been paid to the bio-chemistry of fermentation processes, and it is remarkable that more attention has not been directed to the utilisation for industrial purposes of the organisms which play such an important part in all processes of sewage purification. In this connexion reference may be made to the well-known production of gas in septic tanks, and G. J. Fowler[17] has recently used a " bacterial emulsion " prepared from sludge taken from the bottom of a septic tank for the fermentation of cellulose and hemicelluloses such as banana skins for the production of combustible gas. He has investigated the optimum temperature (35° C.) and the volume and percentage composition of the gas obtained. Another instance of the utilisation of the organisms found in sewage sludge has been described by F. R. O'Shaughnessy[18] in connexion with the de-watering of sewage sludge at Birmingham. The sludge obtained from the sedimentation tanks will not drain readily, and it is therefore mixed with a large proportion of actively fermenting sludge and the mixture allowed to ferment in separate tanks for some months. As a result of this process the nature of the sludge is altered and water separates. The water is decanted, and the sludge is then readily drainable on specially constructed drying beds. By this means the weight of the dry solids in the sludge is reduced by some 30%, and the sludge is disposed of without nuisance. Great care has to be given to the process of mixing the fresh and fermenting sludges, and in cold weather it is necessary to raise the temperature of the mixture by blowing in waste steam.

Since the war, largely as a result of considerations which arose during the war, interest has been revived in the question of the nitrogen in sewage and the possibility of rendering it available for use in agriculture. The Nitrogen Products Committee[19] estimated the nitrogen content of the sewage of the United Kingdom at 234,900 metric tons per annum, of which 86% is present in the urine and 14% in fæces, and indicated that if a method could be found for precipitating the ammonia in sewage a largely untapped source of nitrogen would be opened up. J. J. Dobbie,[20] in his Presidential Address to the Chemical Society, dealing with the war and key industries, and especially with the fixed nitrogen industry, states that no satisfactory method has yet been worked out for obtaining ammonia from sewage on the industrial scale. G. McGowan[21] has presented a very able summary of the problem in a paper read before the Institution of Sanitary Engineers in May. He points out that the nitrogen in human excrement in the United Kingdom amounts to nine times the amount used in the form of sulphate of ammonia and nitrate of soda for agricultural purposes before the war, or to about four times the amount being used now, and that the very small portion of this sewage nitrogen which is being used consists of the more resistant nitrogen compounds, which future investigation should show how to render more readily available for plants. G. J. Fowler,[22] in dealing with the conservation of nitrogen, expresses the opinion that the fundamental economic stability of China depends upon the universal use of human excrement for manure and that the same is true in large measure of Japan. He sees in the activated sludge process a means of restoring from an agricultural standpoint advantages which have been lost by the adoption of the water carriage system of sewage disposal, and there can be no doubt that activated sludge does contain more of the nitrogen of sewage in a more readily available form than any of the forms of sewage sludge hitherto produced.

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[15] *J.*, 1920, 60T.

[16] *J.*, 1920, 177T.

[17] *J. Indian Inst. Sci.*, 1920, 3, 39 ; *J.*, 1921, 22A

[18] *J. Roy. San. Inst.*, 1920, 41, 147.

Another ingenious method of recovering soluble nitrogenous compounds from solutions such as sewage is due to E. H. Richards and H. B. Hutchinson.[23] Their process converts straw into a substitute for farmyard manure, and has been used on the large scale in connexion with the disposal of the urine and slop water from navvies' hutments. A filter of straw is arranged in three layers in such a way that the bottom layer can be removed, the two upper layers lowered, and a fresh layer of straw placed on the top. The sewage is distributed on the top and the fermentation proceeds until the straw has attained a maximum nitrogen content. The bottom layer of straw is then removed and allowed to rot, when it forms an excellent substitute for farmyard manure. The biological processes which underlie the process have been investigated by Richards and Hutchinson and there should be a wide applicability for the process for market gardens which have applicability for the process for large market gardens which have hitherto relied upon stable manure. Supplies of the latter are rapidly diminishing owing to the increasing use of mechanical transport in place of horse haulage.

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[19] *Final Report of the Nitrogen Products Committee, Cmd.* 482. (H.M. Stationery Office, 1920.)

[20] *Chem. Soc. Trans.*, 1920, **117**, 430.

[21] *J. Inst. San. Eng.*, 1920, **24**, 57.

[22] *J. Indian Inst. Sci.*, 1920, **3**, 227.

[23] E.P. 152,387; *J.*, 1920, 827A.

Liquid Trade Refuse.

The problem of treating liquid trade refuse can hardly be said to have made material advances during the year under review, but some ideas which may eventually bear fruit have received a certain amount of experimental investigation.

In the past the methods adopted for the treatment of liquid trade refuse have been in the main adaptations of the methods used either for the purification and softening of water supplies or for the treatment of sewage, and the problems have not been regarded from the distinct viewpoint which their importance warrants. The manufacturer has aimed at getting rid of his refuse at a minimum cost and with as little friction with the Local Authorities as possible. At the present time there is a growing tendency to attempt to use the methods and mechanical appliances which have been used successfully in the industrial processes of the works, and hence the attempts to use centrifugal machines and suction filters which are being made at the present time.

This tendency may be due to present economic conditions which turn the manufacturer's attention to the hitherto neglected possibility of recovering and utilising what he has been in the habit of wasting, but it is also no doubt due to the fact that in many cases he no longer feels assured of an ample water supply for his trade processes. His attention is therefore also directed to the possibility of re-using his liquid trade refuse after purification.

In this connexion the value of such conferences as that on filtration[24] arranged by the Chemical Engineering Group of the Society at the Annual Meeting at Newcastle cannot be appraised too highly, as they afford an opportunity of discussing the relative merits of different plants and obtaining the views of those who have used them for industrial operations. At this conference the centrifugal machines of W. J. Gee and R. A. Sturgeon and the Sharples centrifuge were described and discussed, and it appears likely that these machines will in time find an extended use in the purification of liquid trade refuse. Another machine which should also be applicable for a similar purpose is the " Zenith " rotary filter, which was originally designed for the treatment of gold slimes.

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[24] *J.*, 1920, 226T, 255T.

The activated sludge process of sewage purification has been applied to the treatment of trade waste liquids, but, except in the case of Chicago stockyard refuse, only as yet on an experimental scale. It is understood that the process is to be applied on an experimental scale by the Department of Agriculture and Technical Instruction for Ireland to the treatment of creamery refuse. As in the case of all other methods which have proved effective in the treatment of sewage, it is to be expected that the new process will find application in the treatment of those kinds of trade refuse which are amenable to the ordinary biological purification on percolating filters.

There is at the present time a tendency, fostered during the war, to concentrate the dairy industry in various centres, and the result has been considerable trouble in disposing of the whey and swillings from the dairies. During the war the National Waste Products Co. was preparing to erect a factory in association with the Ministry of Agriculture and Fisheries for the recovery of lactose from whey. This project was abandoned at the termination of hostilities, but the importance of the matter was so great that the Development Commissioners[25] made a grant of £15,000 to the Ministry of Agriculture and Fisheries to proceed with the erection of a demonstration factory. The factory is about to commence operations for the production either of whey solids or of lactose, and it is to be hoped that the results of its working will be such as to demonstrate to farmers the enormous waste which has taken place in the past.

River Pollution.

During the war this subject was much neglected, and the shortage of labour and materials was reflected in the difficulties which were encountered in effecting renewals to plant for the purification of sewage and trade refuse. Sewage precipitants were also very scarce and the use of sulphuric acid for the recovery of grease from sewage and woollen manufacturers' effluents had to be abandoned in spite of the importance and value of the recovered grease in the manufacturing operations. An effective substitute for acid was, however, available in nitre cake,[26] which was produced as a waste product at explosives works and was used to the extent of 6000 tons per month for the recovery of grease. This substance was also used to neutralise the strongly alkaline wastes resulting from the "silicol" process of hydrogen manufacture.

As a result of war conditions the purity of the rivers suffered;

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[25] *Chem. Trade J.*, 1921, 178.

[26] *J.*, 1920, 407R.

more especially in those districts where the rivers were not used as sources of water supply. Nevertheless, much ingenuity was displayed in keeping purification processes going, and the country is to be congratulated that there were no serious epidemics of waterborne disease. In certain districts much damage was done by the discharge of acid waste from explosives works both into sewers and into streams, the plant at the sewage works being eaten away and the effectiveness of sewage filters being seriously impaired. The use of the stream water for steam raising and for manufacturing purposes was attended in some cases with very serious results and considerable amounts of money had to be paid as compensation.

Since the war a certain amount of river purification has been effected, but the more grossly polluted streams in the manufacturing districts are still in a worse condition than in pre-war days, due largely to the slowness in appreciating the altered value of money and the reluctance on the part of Local Authorities and manufacturers to embark upon any expenditure which is not directly remunerative.

Apart from the already mentioned acid discharges, river pollution has not been largely altered in character since the war, but in certain districts it has been accentuated by the establishment of the dye-making industry and by the tendency to concentrate the dairy industry in larger units.

Dairy refuse is of a highly polluting nature, and rapidly gives rise to fungoid growths which, when they decay, create an intolerable nuisance in the streams. As already stated, river pollution from this cause need not arise as the waste products of the dairy industry should be utilised.

Two other industries which are being fostered by the Ministry of Agriculture and Fisheries are the flax industry and the beet sugar industry. Both these industries are potential sources of river pollution and serious complaints have been made of the nuisance caused by flax retting.

The progress of river pollution prevention is seriously hampered by the restrictions which the legislature has imposed upon the Local Authorities responsible for the purification of our streams, and when it is remembered that no general legislation on the subject has been passed since the Rivers Pollution Prevention Act, 1876, it must be apparent that the technical methods of the present day warrant more stringent measures than at that date. Legislation to enable manufacturers to make arrangements for the reception of their trade effluents into the sewers of the Local Authorities and for the purification along with domestic sewage, on the lines recommended by the Royal Commission on Sewage Disposal, is now long overdue.

Towns' Solid Refuse.

In the disposal of towns' solid refuse the keynote of the year has been "salvage," and many towns are at the moment incurring large expenditure which will be either remunerative, or lead to a lower annual expenditure on refuse disposal than has been incurred in the past.

Local Authorities are also endeavouring wherever possible to effect economies in their methods of collection of house refuse, and motor lorries are in many places being substituted for horse haulage.

The large percentage of cinder in house refuse and the possibility of separating this, with the object of obtaining a fuel of a higher calorific value than the refuse as a whole, have been hitherto neglected factors in the problem of refuse disposal. The recovery of waste paper and tins, and the crushing of the rest of the refuse to make a dust which has value as a fertiliser, are also being urged upon Local Authorities by the Ministry of Health. The refuse destructor with its steam-raising capabilities should also not be lost sight of, and it is to be hoped that the insanitary refuse tip will gradually become a thing of the past.

Disinfectants.

Under this heading reference should be made to two new books, viz., "Public Health Laboratory Work (Chemistry)," by H. R. Kenwood[27] and "Organic Medicinal Chemicals," by M. Barrowcliff and F. H. Carr.[28] The latter book forms one of the volumes on Industrial Chemistry, edited by Dr. S. Rideal, and the section on organic antiseptics and disinfectants is a scientific treatise on the subject, which forms inspiring reading.

H. R. Kenwood[29] has urged that the sale of disinfectants should be controlled, so that the efficiency bears some relationship to the price and as a protection to the public, who ought to be in a position to purchase disinfectants which do in fact disinfect. In this connexion the almost invariable use of the Rideal-Walker standard test by Government Departments, Local Authorities, and Railway Companies should be noted.

The plant which was installed for the manufacture of chlorine during the war has found partial utilisation for the production of chlorine for use in the manufacture of halogen disinfectants, and this fact may account for the increasing use of this class of disinfectants as against the phenolic class.

WATER PURIFICATION.

In the purification of water for domestic consumption the outstanding features of the year have been the increasing attention which has been given to the subjects of chlorination and rapid filtration. The former subject has been very ably treated by J. Race in his book on the "Chlorination of Water,"[30] and both subjects have been discussed by Sir A. C. Houston in his Thirteenth Report on Research Work to the Metropolitan Water Board, London.

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[27] Seventh Edition (H. K. Lewis & Co., Ltd., London, 1920).

[28] Baillière, Tindall, and Cox, London, 1920.

[29] *J. Roy. San. Inst.*, 1920, 41, 95.

The chlorination of the London water supply, both the River Thames and New River supplies, has been continued during the year, with the success detailed in last year's Report, and the method of avoiding the "iodoform" taste of chlorinated water by the use of potassium permanganate has also been continuously successful.

J. S. Arthur[31] has described the methods adopted for the chlorination of the water supplied to the armies in the Great War, and especially the use of the Wallace and Tiernan apparatus carried on motor lorries. He states that the use of chlorine gas is now superseding the use of other chemicals for water treatment, and this is to be expected in view of the progress made during the war in the cheapened manufacture of this gas.

The use of chlorinated water has been extended in this country but not to the same extent as in America, where sixty cities with populations of over 100,000 are supplied with chlorinated water according to a report by W. J. Orchard.[32] In this country about a dozen municipal water supplies of any magnitude are chlorinated. Large communities in America have been compelled to adopt indifferent sources of supply and to have recourse to sterilisation, although it would appear that a system of rationing the supply, as described by C. G. Gillespie[33] in connexion with supplies in California, should afford means of conserving the purer waters.

H. W. Clark,[34] the Chief Chemist to the Massachusetts State Department of Health, in a paper read before the New England Waterworks Association, has reviewed the present position of water purification in the United States, and the progress made during the last quarter of a century. Following Drown, he terms waters which are beyond suspicion "innocent" waters, and those which have been purified "repentant." He states that by the provision of proper water supplies the typhoid fever death rate in the United States has been reduced from 45 to 2·6 per 100,000 of the population during the past twenty-five years, mainly by the use of sand filters and chlorine treatment. In the United States 22 millions of the population drink filtered water and chlorination is in use in 2500 cities and towns, but as a purification measure he does not regard chlorination as being in the same class as adequate filtration, and considers that where chlorination is necessary filtration is usually also necessary.

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[30] Chapman and Hall, London, 1920.

[31] *J. Inst. Mech. Eng.*, 1920, 1127 ; *J.*, 1921, 58A.

[32] *San. Rec.*, Sept. 9, 1920, 252.

[33] *Eng. News Rec.*, Sept. 2, 1920, 446.

[34] *Surveyor*, Nov. 26, 1920, 361.

In connexion with the use of chlorinated water the possibility of chemical action on valves and water fittings requires further investigation. Reports from Sacramento, California,[35] indicate considerable corrosion of the valves on the pump suction lines conveying the water which had been dosed with 2·4 lb. of liquid chlorine per million gallons. In this case the difficulty was overcome by moving the point of application of the chlorine further from the pumps. The parts affected were of cast iron; a steel suction pipe was not affected, and the ill-effect on cast iron was attributed to the collection of chlorine gas in the valve bonnets and in high places on the suction line. Inquiries in this country have not revealed any similar ill-effects, but the opinion is held that chlorinated water destroys the ordinary washers on taps.

On the Continent ozone has been used for water sterilisation, and its use has been described by E. K. Rideal[36] in his book on "Ozone (A Treatise of Electro-chemistry)." The subject is also referred to by G. C. Whipple[37] in his report, as Chief of the Sanitation Department of the League of Red Cross Societies, on water supply and disease in Roumania.

With regard to rapid filtration, at the enormously rapid rates of 100 to 200 gallons per square foot per hour, Houston has summarised, in the Research Report already mentioned, the advantages claimed for the process and also the disadvantages urged against it. From his experiments he concludes that the cost of sterilisation, followed by rapid filtration, would be considerably less than the cost of slow sand filtration, and is inclined to condone poor chemical results provided an efficient sterilisation is effected. His experiments have been criticised[38] mainly on the ground of their small scale and the possibility of "slip" or shrinkage at the sides of the filter. The surface shrinkage of rapid filter sand beds has received considerable attention in a paper by A. Wolman and S. T. Powell[39] and in the subsequent discussion[40] in which a large number of American engineers took part, but the differences of opinion expressed only serve to show the necessity for much more scientific investigation.

In one of an admirable series of lectures on chemical engineering problems arranged by the Manchester College of Technology B. Bramwell[41] has described the design of mechanical filters.

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[35] *San. Rec.*, Sept. 23, 1920, 299.

[36] Constable and Co., London, 1920.

[37] *Eng. News Rec.*, Aug. 12, 1920, 305.

[38] *Surveyor*, Sept. 10, 1920, 171.

[39] *Eng. News Rec.*, July 29, 1920, 210; *Surveyor*, Oct. 15, 1920, 245.

[40] *Eng. News Rec.*, Sept. 2, 1920, 438.

[41] *Chem. Age*, Oct. 23, 1920, 442.

The question of the conservation of water supplies has received considerable attention during the year, both in this country and in America. The subject was mentioned in last year's Report, and the Sheffield project for utilising purified River Don water as compensation water is expected to be in operation shortly. The constructional work in connexion with the pumping back of some five million gallons of water daily for a distance of eleven miles is well advanced, and the work has been described by W. Terrey,[42] the Manager of the Sheffield Corporation Waterworks. There can be no doubt that whilst the project is not generally applicable to every waterworks discharging pure water as compensation water, there are other places which will follow the lead of Sheffield, and the effect on the condition of the River Don will be carefully watched when the plant is in operation. The purifying effect of pure compensation water, not only as a diluent of pollution but also as an oxidising agent, has not received sufficient attention in the past.

There can be no doubt that the problem of finding a sufficient water supply of suitable quality for our increasing population and for our increasing trade is becoming acute, and water engineers and sanitarians have for some years been agitating for the setting up of a Central Authority, such as has been advocated by successive Royal Commissions and Departmental Committees, and lastly during the year by the Water Power Resources Committee, to apportion existing sources of supply. The matter formed the subject of a contribution by F. W. Macaulay[43] to the proceedings of the Royal Sanitary Institute during the year. In times of water shortage domestic needs must take precedence over needs for trade purposes, and hence manufacturers would do well to inquire further into the possibility of purifying their trade waste waters for re-use in their trade processes to a much greater extent than they have hitherto done.

In the industrial area of the West Riding of Yorkshire H. M. Wilson has made a survey of the existing sources of water supply, and the results of his investigations have been embodied in Reports presented to the West Riding Rivers Board.

Several gigantic schemes of water supply have been conceived during the year, in which several Local Authorities have combined in order to save the expense of separate undertakings. In this connexion mention should be made of the Southend and South-East Essex Company's scheme[44] and of the South Wales schemes.

In America the problem of providing an adequate supply of pure water is also said to be acute,[45] especially in the Western States, where supplies are needed for irrigation purposes. In some cases the problem resolves itself into a huge engineering undertaking, and it is no uncommon thing to pipe a supply for a distance of two or three hundred miles, but the appointment of a State Commission on Water Supply Needs and Resources[46] is an indication either that the States are taking time by the forelock or that serious difficulties have already arisen.

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[42] *Surveyor*, July 9, 1920, 19.

[43] *Surveyor*, July 30, 1920, 79.

[44] *Eng. News Rec.*, Sept. 2, 1920, 446.

[45] *Surveyor*, Nov. 26, 1920, 361.

The writer is much indebted and wishes to express his thanks to all those, both at home and abroad, who are actively engaged in solving problems connected with sanitation and water purification, for information so readily given about the work upon which they are engaged.

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[46] *San. Rec.*, Dec. 9, 1920, 554.

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FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS.

By T. A. Henry, D.Sc. (Lond.),

Director, Wellcome Chemical Research Laboratories.

The outstanding feature of the year 1920 in connection with the products which come within the purview of this Report, is the steady fall in prices both of raw and manufactured materials. The facts are well known to those interested and there is no need to enlarge on them here, but the following table, which gives the prices of a number of typical drugs and fine chemicals on approximately the same dates in December in each of the years 1913 to 1920, may be of interest as showing the great decline in values since the Armistice, in some cases to prices not far removed from those prevailing in pre-war years.

	1913	1914	1915	1916	1917	1918	1919	1920
Cocaine hydrochloride, per oz.	5/3	7/0	14/6	20/-	50/-	49/- to 50/-	35/-	17/6
Turkey opium, druggists' quality, per lb.	15/- to 15/6	30/-	35/-	38/6	—	68/-	1/6 per unit 19/6–20/0 for 12%	20/-
Morphine hydrochloride, per oz... ..	8/-	13/6	13/6	13/6	13/6	19/6	14/9	—
Quinine sulphate, per oz.	1/1½	1/3	3/6 to 4/6	2/7	3/6	2/11	5/3	4/1
Phenacetin, per lb. ..	2/9	—	60/-	105/-	40/-	17/-	15/-	12/-
Salicylic acid, per lb...	1/-	—	18/6 to 19/-	5/9 to 6/-	6/3	4/-	2/6 to 2/8	2/-
Menthol, per lb. ..	10/- to 10/6	11/3	11/6	14/0	13/6	20/6	66/-	27/6
Thymol, per lb. ..	6/-	21/6	45/-	32/6	45/-	47/6	38/-	40/-

The table also illustrates the importance to a country of a fine chemical industry. Comparing the changes in value of cocaine hydrochloride, which was not manufactured in this country before the war, and is still not made here on an adequate scale, and those of morphine hydrochloride, of which our home-made supplies have always been sufficient, it will be seen that while the former rose to something like ten times its value during the war, morphine hydrochloride showed a comparatively small advance in price. In the case of morphine the raw material, opium, and the extraction of the alkaloid are under British control; in the case of cocaine both were under foreign control. Quinine is an intermediate case; here the raw material is in the hands of a foreign country but the alkaloid is extracted in this country, though not on a scale large enough to meet home requirements, and the price rose considerably, though not to the same extent as that of cocaine. These three alkaloids are merely examples of a number of medicinal chemicals which are essential to the welfare of the population in peace and war, and nothing should be left undone to provide within the Empire large enough supplies of the necessary raw materials for their production and to secure the means for their manufacture at home on a scale sufficient to meet at least the Empire's requirements of the manufactured products.

ALKALOIDS.

Cinchona alkaloids.

Perhaps the most important paper in connexion with cinchona alkaloids published during the year is that of Major H. Acton[1] dealing with the therapeutical value of the different alkaloids. Opinion has been greatly divided for years past as to the value of the alkaloids quinidine, cinchonine, and cinchonidine, which accompany quinine in cinchona bark, in the treatment of malaria, some authorities being of opinion that quinidine is better than quinine, and cinchonine and cinchonidine of less value, whilst others maintain that a mixture of all of them, usually given in the form of a purified extract of *Cinchona Succirubra* bark (Cinchona febrifuge), is better than quinine alone. Major Acton's results appear to offer at least a partial explanation of these anomalies, since he shows that the benign and malignant tertian types of malaria respond best to treatment with different alkaloids, benign to quinidine or cinchonidine and malignant to quinine or cinchonine. Cinchonine is not a good substitute for quinine as it is distinctly more toxic. These results have considerable practical possibilities and they emphasise once more the difference in physiological action exhibited by optical isomerides (not necessarily optical antipodes), a subject to which Prof. Cushny has given much attention in this country. Allusion was made in the previous report[2] to the proposal to extend cinchona cultivation in India, and in carrying out this project it will be desirable to take Major Acton's work into account and, instead of planting solely for the production of quinine, as has been the practice hitherto, to adopt a scheme which will provide quinine and quinidine and possibly cinchonidine.

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[1] *Brit. Med. J.*, July 24, 1920, 117; *Lancet*, 1920, **198**, 1251; *Cf.* P. Hehir, *ibid.*, 1382.

The aftermath of the war no doubt accounts for the prominent place occupied by quinine and the related bases in the work done on alkaloids during 1920, which includes numerous observations on the use of quinine in malaria and other diseases, methods of administering the alkaloid and of increasing its efficacy, and investigations of its behaviour in the body and the form in which it is eliminated. So far as purely chemical investigations on cinchona alkaloids are concerned reference may be made to the continuation of the work of W. A. Jacobs and M. Heidelberger,[3] which has included the preparation of (1) a number of quaternary salts of the alkaloids, with a view to the study of their bactericidal and especially their pneumococcicidal properties, (2) an extensive series of azo-dyes from hydrocupreine and hydrocupreidine, (3) nitro and amino derivatives of the same alkaloids and of hydroquinine and hydroquinidine, and (4) dihydrodeoxyquinine and the corresponding quinidine compound and a few of their derivatives. As regards (3) similar work has been completed by G. Giemsa and J. Halberkann[4] in Germany, who included hydrocinchonine and hydrocinchonidine.

Opium and its Alkaloids.

H. E. Annett[5] has published a preliminary account of the combined botanical and chemical investigations undertaken in India with a view to increasing the alkaloidal content of the opium produced there and so rendering it more suitable for use in medicine and the manufacture of morphine and codeine. The points so far established are as follows :—The yield of latex and its morphine content fall with each successive tapping of the poppy head; thus in a typical case, where the same set of poppy heads was tapped in succession six times, the percentages of morphine in the dry opium obtained were 13·9, 9·6, 5·8, 3·6, 2·2, 1·6. The amounts of narcotine and codeine do not fall off to the same extent and may even increase in certain of the later lancings, and on the whole they are less regular in their behaviour than that of morphine. When the latex is collected in fractions on the same day there is a falling off in alkaloidal content from the first to the last fraction, but on similar fractional treatment on subsequent days the alkaloidal content of the first fraction is higher than that of the last fraction of the previous tapping, but again declines in the later fractions of the second lancing. An increase in the number of incisions from 1 to 3 at each lancing gives a slight increase in the yield of latex. The terminal capsules invariably give more latex than the lateral capsules. The store of latex in the capsule is at a maximum when the latter is firm and of full size (15 to 17 days after flowering) and the morphine content of the latex attains its maximum about 9 days after flowering. Climate has a slight influence on the yield of morphine: thus in 1919–20 the percentage of morphine obtained from opium produced at five different stations in India varied as follows:—Cawnpore 15·4, Rae Bareli 13·1, Fatehgarh 16·6, Etawah 16·8, Douglas Dale 14·0. Seasonal variations affect the yield at least as much as climatic differences, and slight disturbances are produced by varying weather conditions during the collecting season, the yield of latex diminishing with a rise in temperature and *vice versâ*, though the yield of morphine remains fairly constant throughout the season. Nitrogenous manuring increases the size of the plants and of the poppy heads produced and so increases the yield of latex, but the percentage of morphine is only slightly improved. The author finally draws the conclusion that in the opium poppy, morphine is an end product of metabolism, which, since it cannot be excreted, is stored in the walls of the capsule.

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[2] *Ann. Repts.*, 1919, **4**, 489.

[3] *Ann. Repts.*, 1919, **4**, 490; *J. Amer. Chem. Soc.*, 1919, **41**, 2090, 2131; 1920, **42**, 1481 (*cf.* G.P. 283,537), 1489.

[4] *Ber.*, 1920, **53**, 732.

[5] *Biochem. J.*, 1920, **14**, 618.

It is clear from these results that by suitable modifications of the processes of collection and preparation it will be possible to produce in India opium at least as rich in morphine and richer in codeine than the average opium at present obtained from Turkey and Persia.

In connexion with this work a new method for the estimation of codeine in opium has been devised.[6]

Important papers dealing with the constitution of morphine and codeine have been published by J. von Braun[7] and by M. Freund, W. W. Melber, and E. Schlesinger.[8]

Other Alkaloids.

Prof. E. Perrot and M. Alland,[9] who are investigating the possibility of developing in the French Colonies the production of drugs, have published a report on a visit to Egypt and the Anglo-Egyptian Sudan, where they inquired into the gum industry, the cultivation of senna, and the production of Egyptian henbane (*Hyoscyamus muticus*), datura, colocynth, and other drugs, of which henbane is by far the most important, having become the chief source of atropine sulphate. It is satisfactory to find that the bulk of the henbane exported from this territory is now finding its way to this country. The possibility of producing atropine synthetically is not being lost sight of, processes for the preparation of tropic acid[10] and a tropine homologue[11] having been described and in some cases protected, whilst R. Willstätter[12] has patented the preparation of (1) succinyldiacetic esters for use in the synthesis of tropine derivatives, the final product in this first stage being dimethyl-N-methylpyrrolidine diacetate, and (2) the preparation from the product just named of tropinonecarboxylic esters from which tropinone and ecgonine can be made. In view of the fact that atropine does not occur as such in solanaceous plants, but is made by racemisation from the *l*-hyoscyamine present, surprise is sometimes expressed by chemists that the *lævo* alkaloid, which is much more active physiologically than the *dl*-form, atropine, has not replaced the latter for producing cycloplegia in routine refraction work. According to N. Bishop Harman,[13] when hyoscyamine was tried some years ago it gave rise to secondary toxic effects and for that reason he recommends medical men to restrict themselves to atropine and homatropine, the latter being used where rapid and transient action is required and the former to produce a slower but more sustained effect. As *l*-hyoscyamine is more active than atropine in producing mydriasis, it should be used in correspondingly smaller quantity.

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[6] H. E. Annett and H. Sen, *Analyst*, 1920, **45**, 321; *J.*, 1920, 702A.

[7] *Ber.*, 1919, **52**, 1999.

[8] *J. prakt. Chem.*, 1920, ii., **101**, 1.

[9] *Pharm. J.*, 1920, **105**, 488.

J. von Braun[14] and his collaborators are continuing their investigation of the influence on pharmacological action of the displacement of certain specific groups and linkages in the tropeine and cocaine groups of alkaloids. In these two groups the factor conditioning physiological action appears to be the presence of an acylated hydroxyl group in the γ-position to the nitrogen atom The results so far obtained are insufficient to warrant genera conclusions being drawn, especially with regard to mydriatic action but the maximum of anæsthetic action seems to be reached when the -OH group is in the γ-position to the nitrogen and within this limitation the mode of attachment of the hydroxyl within the molecule appears to be unimportant. Ethylenic linkages within the 7-carbon ring increase the anæsthetic action.

Interesting papers on scopoline (oscine), the basic hydrolyti product of hyoscine (scopolamine), and on cuskhygrine, one of the secondary alkaloids of coca leaves, have been published by K Hess.[15]

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[10] *Ann. Repts.*, 1918, **3**, 443; 1919, **4**, 491; *cf.* A. McKenzie and J. Wood ., 1919, 654A; J. von Braun, *Ber.*, 1920, **53**, 1409.

[11] E. Muller, U.S.P. 1,352,082; *J.*, 1920, 734A.

[12] G.P. 300,672 and 302,401: *J.*, 1920, 385A, 583A.

[13] *Brit. Med. J.*, May 1, 1920, 598.

[14] *Ber.*, 1920, **53**, 601. *Cf.* Von Braun and Muller, *Ber.*, 1918, **51**, 235.

J. Gadamer[16] has investigated the three alkaloids chelidonine and α- and β-homochelidonines, and shown that the two former are closely allied, whilst β-homochelidonine belongs to the protopine group. Constitutional formulæ are assigned to all three alkaloids. P. J. Hanzlik[17] has called attention to the value of chelidonine as a possible substitute for papaverine.

A developed form of the process described in the previous report for the synthesis of hydrastinine homologues has been patented by K. W. Rosenmund[18]: these products are stated to be less toxic than hydrastinine.

J. Abelin[19] has described a number of complex compounds of the calcium salts of acetylsalicylic acid (aspirin) and of ω-methylsulphonic acids of *p*-phenetidine, 4-amino-antipyrine, etc., with caffeine, theobromine, and theophylline, which are said to be freely soluble in water and of therapeutic value. Double compounds of caffeine with alkali salts of acetylsalicylic acid have been patented.[20]

Among the minor alkaloids, K. Hess and H. Mohr[21] have shown that sabadinine is identical with cevine and have re-described several simple derivatives of the alkaloid. Ormosine, $C_{20}H_{33}N_3$, and its isomeride ormosinine (possibly anhydrous ormosine) are two new alkaloids from *Ormosia dasycarpa*, described and characterised by K. Hess and F. Merck.[22] The former resembles morphine in physiological action, but is not allied to it chemically.

The alkaloid aribine, described by Rieth in 1861, proves to be identical with harman, a substance already produced from harmine and from tryptophan.[23]

K. Gorter[24] finds that the alkaloid narcissine, described by Ewins, is identical with lycorine, obtained ten years earlier from *Lycoris radiata* by Morishima, and has also proved its occurrence in a number of other plants of the order *Amaryllidaceæ*.

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[15] *Ber.*, 1919, **52**, 1947; K. Hess and H. Fink, *Ber.*, 1920, **53**, 781.

[16] *Arch. Pharm.*, 1919, **257**, 298; *J.*, 1920, 80A, 762A; *Cf.* Momoya, *J. Pharm. Soc. Japan*, 1919, No. 44, 110.

[17] *J. Amer. Med. Assoc.*, 1920, **75**, 1324.

[18] *Ann. Repts.*, 1919, **4**, 492; G.P. 320,480; *J.*, 1920, 675A.

[19] *Apoth.-Zeit.*, 1919, **34**, 316.

[20] Chem. Fabr. J. A. Wülfing, E.P. 136,187; *J.*, 1920, 135A.

[21] *Ber.*, 1919, **52**, 1984; *J.*, 1920, 80A.

[22] *Ber.*, 1919, **52**, 1976; *J.*, 1920, 80A.

[23] E. Späth, *Monatsh.*, 1919, **40**, 351; *cf. Ann. Repts.*, 1919, **4**, 492; *J.*, 1920, 312A.

[24] *Bull. Jard. Bot. Buitenzorg*, 1920, iii., **1**, 352; **2**, 331; *cf.* Ewins, *Trans. Chem. Soc.*, 1910, **97**, 2406; Tutin, *ibid.*, 1911, **99**, 1240; Morishima, *J. Chem. Soc.*, 1899, **76**, 92.

SIMPLE NATURAL BASES.

Thyroxine, the hormone of thyroid gland, which was isolated and synthesised by E. C. Kendall,[25] has now been placed on the market by a firm in the United States.

The discussion as to the identity of the physiologically active component of the hypophysis with histamine, first advanced by J. J. Abel and S. Kubota,[26] continues. H. Dudley, D. Cow, and others find no evidence of the presence of histamine and that there is considerable difference in the physiological action of histamine and the gland product.[27] J. J. Abel and T. Nagayama[28] find that extracts made from fresh glands, taking special precautions to avoid decomposition during manufacture, contain a small amount of histamine, but the quantity is much less than is present in commercial pituitary extracts, and they appear to attribute the excess present in the latter to decomposition of protein during manufacture. The issue has, therefore, now been narrowed to the question whether histamine occurs in the fresh gland at all.

G. Barger[29] has given an interesting account of the chemistry of ergot and of the history of this material, both in relation to the causation of " ergotism " and its use in medicine. During the war there seems to have been considerable difficulty in obtaining adequate supplies of ergot in Germany, and the drug appears to have been replaced partly by extracts of shepherd's purse[30] and partly by special preparations, two of which, " tenosin " and " metrotonin," have been referred to lately in the German medical press. " Tenosin "[31] is stated to be a mixture of *p*-hydroxyphenylethylamine (" tyramine ") and β-ethylaminoglyoxaline (" ergamine "). A British synthetic preparation containing these two constituents, which are components of ergot, and in addition ergotoxine, the characteristic alkaloid of the drug, has been on the market for many years. " Metrotonin "[32] is a complex mixture stated to contain, among other things, sparteine and acetylcholine. Processes for the extraction of the active constituents of ergot have recently been protected.[33]

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[25] *Ann. Repts.*, 1919, **4**, 493 ; *J. Amer. Med. Ass.*, 1920, **74**, 104.

[26] *Ann. Repts.*, 1919, **4**, 493.

[27] H. Dudley, *J. Pharm. Exp. Ther.*, 1919, **14**, 295 ; D. Cow, *ibid.*, 275 ; M. T. Hanke and K. K. Koessler, *J. Biol. Chem.* 1920, **43**, 337 ; D. E. Jackson and C. A. Mills, *J. Lab. Clin. Med.*, 1919, **5**, 1 ; *cf. J. Amer. Med. Ass.*, 1920, **75**, 1424.

[28] *J. Pharm. Exp. Ther.*, 1920, **15**, 347, 401 ; *J.*, 1920, 673A ; *cf.* J. J. Abel and D. Macht, *ibid.*, 1920, **15**, 279 ; and M. T. Hanke and K. K. Koessler, *loc. cit.*

[29] *Pharm. J.*, 1920, **205**, 471.

[30] H. Borattu, *Deuts. Med. Woch.*, 1920, **46**, 210 ; Grimme, *Pharm. Zentralh.*, 1919, **60**, 238.

[31] F. Jaeger, *Z. Gynäkol.*, 1919, No. 29 ; *Chem. Zentr.*, 1920, I., 232.

[32] H. Borattu, *Deuts. Med. Woch.*, 1920, **46**, 969 ; *Chem. Zentr.*, 1920, IV., 514.

Salts of choline and its homologues with boric, salicylic, formic, and *p*-aminophenylarsinic acids are stated to have the same action as choline itself, but to be more certain owing to their greater stability, and are suggested for use in the treatment of tumours; salts with dihalogenated hydroxybenzoic acids are said to be non-hygroscopic.[34]

Several interesting papers on glyoxaline, which is the nucelus of a number of natural bases of importance in medicine and in bio-chemistry, have been published.[35] F. L. Pyman and L. A. Ravald have succeeded in sulphonating glyoxaline, probably in the 4-position, and have obtained good yields of the sulphonic acid under conditions which are specified in their paper.[36] An interesting substance in this series has been prepared by O. Gerngross and H. Nast,[37] viz., 4-β-*p*-hydroxyphenylethyl-β-aminoethylglyoxaline, which contains the residues of two of the active constituents of ergot, tyramine and ergamine.

GLUCOSIDES.

Though only one paper[38] has been published during the year dealing with the chemistry of digitalis, much work has been done, chiefly with regard to methods of ensuring uniformity in the strength of digitalis preparations[39] and on the therapeutics of the drug,[40] especially in the United States. Some of the pharmacological papers deal with the action of squills and strophanthus in comparison with that of digitalis. In so far as they relate to the chemistry of digitalis these papers do little to remove the prevailing confusion; thus, while two of the authors regard the saponins present in digitalis leaf as toxic, a third finds them inert, and one apparently takes the view that the leaves contain digitonin, whilst another points out that the latter only occurs in the seed.

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[33] Sandoz Chemical Works, E.P. 125,396; *J.*, 1920, 349A; Soc. Chem. Ind. Basle, G.P. 317,400.

[34] Verein. Chem. Werke E.P. 8031, 1914; *J.*, 1920, 43A; F. Hoffman-La Roche & Co., G.P. 290,523; *J.*, 1916, 558.

[35] R. G. Fargher, *Chem. Soc. Trans.*, 1920, **117**, 668; F. L. Pyman and L. A. Ravald, *ibid.*, 1426.

[36] *Chem. Soc. Trans.*, 1920, **117**, 1429.

[37] *Ber.*, 1919, **52**, 2304.

[38] H. Kiliani, *Ber.*, 1920, **53**, 240; *J.*, 1920, 278A.

[39] E. Berry, *Pharm. J.*, 1919, **103**, 69; J. H. Pratt and H. Morrison, *J. Amer. Med. Ass.*, 1919, **73**, 1606; H. F. West and J. H. Pratt, *ibid.*, 1920, **75**, 77; H. H. Meyer, *Wien. Med. Woch*, 1920, **70**, 11; G. Joachimoglu, *Berl. Klin. Woch.*, 1919, **56**, 1212; *cf. J.*, 1920, 557A, 762A; G. Focke, *Arch. Pharm.*, 1919, **257**, 270; A. Maisel, *Münch. Med. Woch.*, 1920, **67**, 803; W. J. McGill, *J. Amer. Chem. Soc.*, 1920, **42**, 1893; *J.*, 1920, 703A; C. A. Pomeroy and F. W. Heyl, *Amer. J. Pharm.*, 1920, **92**, 394; *J.*, 1920, 581A; H. C. Hamilton, *ibid.*, 529 and *J. Ind. Eng. Chem.*, 1920, **12**, 1180; T. S. Githens, *J. Amer. Pharm. Ass.*, 1920, **9**, 1060; L. W. Rowe and R. A. Hatcher, *ibid.*, 900, 913.

[40] H. E. Pardee, *J. Amer. Med. Ass.*, 1919, **73**, 1822; 1920, **75**, 1258; Edit., *ibid.*, 1920, **74**, 544; **75**, 417; L. M. Warfield, *ibid.*, 1920, **75**, 1453; P. D. White, G. M. Balboni, and L. E. Viko, *ibid.*, 1920, **75**, 971; S. Loewe, *Deuts. Med. Woch.*, 1919, **45**, 1433; A. Jarisch, *Berl. Klin. Woch.*, 1919, **55**, 1235; H. Roberburg, *Münch. Med. Woch.*, 1920, **67**, 152.

K. Gorter[41] has isolated an interesting glucoside from *Hiptago madablota*, which is named hiptagin, $C_{10}H_{14}O_9N_2$ and has the peculiar property of yielding ammonia and hydrocyanic acid on treatment with dilute alkali, whilst with dilute sulphuric acid dextrose and tartronic acid are produced. The substance has been exhaustively investigated, and a constitutional formula representing it as an iso-oxazole derivative is proposed.

ESSENTIAL OILS.

A considerable number of publications of interest to the essential oil industry have appeared recently, including a dictionary of odoriferous substances[42] and a treatise on distillation,[43] both by T. H. Durrans, a book on the pharmacology of essential oils by D. Cow, a series of articles on the manufacture of synthetic perfumes by G. Chazel,[44] and two papers by R. Greig Smith[45] on the germicidal action of eucalyptus oils.

It seems clear from the advertisements which appear in the technical press that the list of synthetic aromatic products made in this country is being steadily, if slowly, extended, and there are many recent developments in the production of essential oils in the British Dominions and Colonies. In Australia the distillation of eucalyptus oils is no longer restricted to those containing cineol, but the oils yielding citronellol, geranyl acetate, and piperitone are also being produced and the pure oil constituents, cineol, phellandrene, piperitone, geranyl acetate, and citronellol either are being made or their production is about to be undertaken. Considerable attention is also being given to the distillation of a sandalwood oil from *Fusanus spicatus* in West Australia, though it still remains to be ascertained whether this contains santalol and can be legitimately used especially in medicine, in place of the Indian oil from *Santalum album.*

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[41] *Bull. Jard. Bot. Buitenzorg*, 1920, iii., 2, 187; *J. Chem. Soc.*, 1920, **118**, i., 624.

[42] *Perf. Essent. Oil Rec.*, 1920, **11**, 45, 79, 113, 258.

[43] *Ibid.*, *Special number*, p. 154.

[44] *Rev. Prod. Chim.*, 1918, **21**, 307, 328, 349, 372, 397, 409; 1919, **22**, 63, 89, 177, 201, 559.

[45] *Proc. Linn. Soc. N.S.W.*, 1919, 72, 311.

In India, whence, before the war the whole crop of ajowan seed was exported to Germany for the production of thymol, the seed is now being distilled locally, and for the two years ending June, 1919, the exports of thymol amounted to over 10,000 lb.[46] The distillation of sandalwood oil has apparently been very successful in Mysore, and a number of the commoner spices such as dill, coriander, clove, etc., are now being distilled in India and the oils exported to this country. The production of rose oil has been taken up on a small scale in Cyprus[47] and a project is under way for the distillation of clove oil in Zanzibar,[48] whilst in Jamaica arrangements are being considered for the distillation of pimento leaves and possibly the manufacture of vanillin from eugenol extracted from the oil.[49]

Similar developments are desired in France and the French Colonies, and an association has been formed to encourage the cultivation of drugs and essential oil plants, under whose auspices a study has been made of lavender cultivation in France.[50]

The Government of Italy has established an industrial experiment station for the oil and perfume industry, which aims at introducing new processes, new applications for products, and the training of an expert personnel for the industry.

Perhaps the most interesting paper on essential oils published during the year is that by J. L. Simonsen [51] on Indian turpentine oil derived from *Pinus longifolia*, Roxb. In 1911 H. H. Robinson stated that the principal component of the oil is a terpene, which, though not sylvestrene, yields sylvestrene hydrochloride. Simonsen has now shown that on treatment with hydrogen chloride dipentene is produced as well as sylvestrene, and on this and other evidence regards it as a bicyclic terpene, probably either d-Δ^3-, or d-Δ^4-carene, so that it appears to be the first known naturally occurring terpene containing the carane ring.

The high-boiling constituent of the oil is a new sesquiterpene, longifolene, of which a number of crystalline derivatives have been obtained. *Pinus longifolia* Roxb. is the chief source of the turpentine oil distilled in India, an industry which in recent years has made rapid progress, the output being now almost equal to India's own requirements and likely to afford in the near future a surplus for export.

The output of camphor and camphor oil in Formosa, the principal source of supply, has been diminishing in the last few years, owing, it is stated, to scarcity of labour.[52] As a consequence increased attention is being given to the production of camphor in India and Burma,[53] the United States, and elsewhere, where plantations already exist, but where production has hitherto not been largely developed owing to the abundance and cheapness of the far Eastern supplies. In the United States the cost of labour is the chief difficulty, and attempts are being made to overcome this by the use of a mechanical clipper[54] for cutting the leaves and twigs used for the distillation. It is also stated that the present price of camphor allows of the profitable extraction of the latter from rosemary and other oils not hitherto used for this purpose.[55]

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[46] *Perf. Essent. Oil Rec.* 1920, **11**, 104.

[47] Bevan, *Bull. Imp. Inst.*, 1919, **17**, 507.

[48] *Perf. Essent. Oil Rec.*, 1920, **11**, 91.

[49] *Bull. Imp. Inst.*, 1919, **17**, 297 ; *Perf. Essent. Oil Rec.*, 1920, **11**, 31, 268, 295.

[50] *Ibid.*, 251, 275.

[51] *Chem. Soc. Trans.*, 1920, **117**, 570 ; *J.*, 1920, 581A.

Along with these efforts the United States especially is endeavouring to increase the supply of synthetic camphor,[56] and a number of patents have been taken out dealing with (1) the separation by "baking" of the last traces of oil in the purification of camphor,[57] and (2) the conversion of isoborneol into camphor by oxidation with nitric acid, alone, or in presence of sulphuric acid or a halogen and with or without the assistance of an electric current or heat.[58]

Extended reference was made in the previous report[59] to the efforts made to find an outlet for *p*-cymene obtainable from spruce turpentine, produced as a by-product in the sulphite-cellulose industry. Other sources of cymene are waste terpenes from the manufacture of camphor, and pine-needle oil residues.[60] A. S. Wheeler describes a method suitable for laboratory use for the preparation of cymene from spruce turpentine and discusses its possibilities as a solvent, and in this connexion gives an extensive series of solubilities of organic compounds in the liquid.[61] The preparation of derivatives of cymene, mostly dyes, is the subject of a series of patents by C. E. Andrews.[62]

A further method of making thymol from cymene has been protected: it consists in nitrating the hydrocarbon, reducing the nitro-compound to cymidine, sulphonating, removing the

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[52] *Perf. Essent. Oil Rec.*, 1920, **11**, 300; *cf. J.*, 1920, 76R, 306R.

[53] J. L. Simonsen and T. P. Ghoze, *J.*, 1920, 296T; *cf. J.*, 1920, 379R.

[54] *Perf. Essent. Oil Rec.*, 1920, **11**, 226.

[55] *Ibid.*, 89.

[56] *J.*, 1920, 236R.

[57] E. I. du Pont de Nemours & Co., E.P. 124,413; *J.*, 1919, 657A; The Arlington Co., U.S.P. 1,308,398; *J.*, 1919, 657A; *cf. J.*, 1918, 636A. E.P. 124,704; *J.*, 1920, 696A.

[58] E. I. du Pont de Nemours & Co., U.S.P. 1,313,661; *J.*, 1919, 794A; U.S.P. 1,324,140; *J.*, 1920, 135A; U.S.P. 1,326,248; *J.*, 1920, 174A; U.S.P. 1,347,071; *J.*, 1920, 611A.

[59] *Ann. Repts.*, 1919, **4**, 111, 496.

[60] Rheinische Kampferfabr. Ges., E.P. 142,738; *J.*, 1920, 501A.

[61] *J. Amer. Chem. Soc.*, 1920, **42**, 1842; *cf. J.*, 1920, 703A; *cf.* L. Akerbloom, U.S.P. 1,333,694; *J.*, 1920, 361A.

[62] U.S.P. 1,314,920—1,314,929; *J.*, 1919, 813A; *Chem. Abs.*, 1919, 2765.

NH_2-group by diazotisation, and finally fusion of the residual sulphonic acid with alkali.[63]

H. G. Smith and A. R. Penfold[64] have called attention to the possibility of making thymol, menthone, and menthol from piperitone, the ketone found in the oils from various species of eucalyptus but especially *E. dives*, the leaves of which yield from 3 to 4% of oil containing 40–50% of piperitone, the rest being chiefly phellandrene, which can be used in the flotation process for the separation of minerals. On oxidation with ferric chloride piperitone yields thymol, and on reduction with hydrogen in presence of a nickel catalyst at 175°–180° C. is converted nearly quantitatively into menthone, which in turn can be reduced to menthol.

Two processes for the production of vanillin have been patented In the first, molecular quantities of guaiacol and formaldehyde in alcohol are heated at 100° C. with half a molecular proportion of *p*-nitrosodimethylaniline and hydrochloric acid, hydrogen chloride being passed through the mixture. Along with vanillin there is produced *p*-aminodimethylaniline. The process is also applicable to anisaldehyde, protocatechuic aldehyde, and various hydroxy-aldehydes.[65]

In the second process acyl or aryl derivatives of vanilloyl chloride, made by the action of the appropriate acyl or aryl chloride on vanillic acid, and conversion of the products into the corresponding chlorides with thionyl chloride, are treated in toluene or xylene at boiling temperature with hydrogen in presence of a catalyst, such as palladium or nickel. The products are the corresponding vanillin esters or ethers, which may then be hydrolysed in the ordinary way.[66]

SYNTHETIC DRUGS.

The critical stage through which the fine chemical industry is passing probably accounts for the paucity of patents for synthetic drugs in 1920. Such patents as have been taken out are chiefly for modifications in the manufacture of well known preparations or for slight variants on products of well known types. A useful résumé of existing knowledge of synthetic drugs was given by J. T. Hewitt in a series of lectures to the Royal Society of Arts.[67]

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[63] M. Phillips, U.S.P. 1,332,680; *J.*, 1920, 528A, 639A; *cf. Ann. Repts.*, 1919, 4, 497.

[64] *Proc. Roy. Soc. N.S.W.*, 1920, **54**, 40.

[65] A. Weiss, E.P. 139,153; *J.*, 1920, 527A.

[66] Confectionery Ingredients, Ltd., F. E. Matthews, A. T. King, and T. Kane, E.P. 131,161; *J.*, 1919, 740A; *cf. J.*, 1920, 640A.

[67] *J. Roy. Soc. Arts*, 1920, **68**, 625, 639.

Hypnotics.

The attempts to improve on "veronal" (diethylbarbituric acid) referred to in a previous report still continue, and among the new preparations is dibutylbarbituric acid, claimed to combine pronounced sedative properties with low toxicity.[68] Diallylbarbituric acid has been tested by the experts of the American Medical Association and found to have a higher toxicity than chloral hydrate or veronal and to cause, like other hypnotics, lowering of blood pressure and depression.[69]

On condensing bromacylised carbamides with acylising reagents in presence of sulphuric acid or zinc chloride, compounds are produced which are stated to exert a rapid but lasting sedative and hypnotic action. In this way acetylbromo-α-ethylbutyrylcarbamide is obtained by the interaction of acetic anhydride and bromo-α-ethylbutyrylcarbamide in presence of zinc chloride. A number of homologues have also been prepared and described.[70]

The preparation of a series of *p*-carbamidophenylacylcarbamides and related compounds has been commenced with a view to the examination of their physiological action, especially as hypnotics.[71]

A. Lumière and F. Perrin have given a preliminary description of diethyl-, ethylpropyl-, dipropyl-, and diallyl-homophthalimides prepared by the action of the corresponding alkyl iodides on homophthalimide, in presence of sodium ethoxide. They are stated to possess hypnotic properties, to be only slightly toxic, and to be free from unfavourable secondary action.[72]

Local Anæsthetics.

There has been considerable activity in the investigation of local anæsthetics, principally in the United States and chiefly on the pharmacological side, partly on the general question of their mode of action and partly on the comparison of the toxicity and secondary effects of the better known drugs. Work on the latter subject is of considerable interest as there is a good deal of conflicting information regarding the toxicity of some well known products of this group. Certain of the best known local anæsthetics have, according to C. Eggleston and R. A. Hatcher,[73] the following absolute toxicities as tested on cats:—Alypine, holocaine, 10; β-eucaine, 12·5; cocaine, 15·0; apothesine, 20·0; tropacocaine,

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[68] O. Kamm and E. H. Volleweiler, U.S.P. 1,331,712; *J.*, 1920, 764A.

[69] *J. Amer. Med. Ass.*, 1920, **74**, 266.

[70] Farbenfabr. vorm. F. Bayer u. Co., E.P. 132,795; *J.*, 1920, 280A.

[71] M. Rising, *J. Amer. Chem. Soc.*, 1920, **42**, 128; *J.*, 1920, 425A.

[72] *Comptes rend.*, 1920, **171**, 637; *J.*, 1920, 763A.

[73] *Proc. Soc. Exp. Biol. Med.*, 1918, **16**, 16; *J. Pharm. Exp. Ther.*, 1919, **13**, 433; *cf.* T. Sollmann, ibid., 1917, **10**, 379; 1918, **11**, 69; H. C. Hamilton, *J. Lab. Clin. Med.*, 1918, **4**, 60; *J. Amer. Med. Ass.*, 1920, **74**, 266.

20–25; stovaine, 25–30; nirvanin, 30–35; novocaine, 40–45. L. Launoy and Y. Fujimori[74] have compared the toxicity, hæmolytic power, and anæsthetic properties of a number of derivatives of the amino-alcohols represented by the formulæ $Me_2N.CH_2.CR(OH).CH_3$ and $Me_2N.CH_2.CH_2.CH(OH)R$. E. Fourneau and J. Ranedo[75] have examined the physiological effect of the replacement of a phenoxy- by an anilino-group in amino-alcohols derived from aniline and its homologues. While stovaine (benzoylethyldimethylaminopropyl alcohol hydrochloride) in $N/25$ solution acts in 4 to 5 minutes, benzoylmethylanilinodimethylaminoisopropyl alcohol hydrochloride in $N/25$ solution only acts in 17 minutes.

E. A. Wildman[76] has patented a series of derivatives of aminotoluic and alkyloxyaminobenzoic acids, including diethylaminoethyl 3-amino-*p*-toluate and diethylaminoethyl *m*-aminoanisate. They yield crystalline hydrochlorides, which are stated to act as anæsthetics and to possess but little irritant or toxic action.

O. Kamm[77] has prepared two substances closely allied to the foregoing, viz., *p*-diethylaminopropyl *p*-aminobenzoate and its *p.m*-isomeride. The hydrochloride of the former is said to be intermediate in action between cocaine and novocaine, and to be slightly more toxic but more efficient as a surface anæsthetic than the latter.

J. Altwegg and J. Landrivon[78] have protected the preparation of alkylaminoethylaminobenzoates of the type $Et_2N.CH_2.CH_2.NH.C_6H_4.COOEt$ and halogen-ethylaminobenzoates such as $CH_2Cl.CH_2.NH.C_6H_4.CO_2Et$ for use as local anæsthetics.

J. von Braun and G. Kirschbaum find that aromatic substitution at the nitrogen atom of novocaine is without influence on the anæsthetic power if the basicity of the molecule as a whole is suitably increased.[79]

A good deal of interest has been aroused by D. I. Macht's[80] discovery that benzyl alcohol is a useful anæsthetic; the same property seems to be exhibited by the homologues, phenylethyl alcohol[81] and salicylic alcohol[82] and to a less extent by benzaldehyde.[83] Arising out of this work a use has been found for benzyl benzoate[84] especially as an antispasmodic, and the material has been placed on the market in the United States and in this country for this purpose. G. Laurens recommends guaiacol[85] as an anæsthetic for minor operations on the ear, nose, and throat.

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[74] *Comptes rend. Soc. Biol.*, 1919, **82**, 732; *J.*, 1920, 81A.

[75] *Anal. Fis. Quim.*, 1920, **18**, 133; *J. Chem. Soc.*, 1920, **118**, i., 672.

[76] U.S.P. 1,317,250–1; *J.*, 1920, 426A.

[77] *J. Amer. Chem. Soc.*, 1920, **42**, 1030; *J.*, 1920, 500A.

[78] E.P. 128,552–4, U.S.P. 1,344,641–2; *J.*, 1920, 380A; *cf. J.*, 1920, 43A, 280A; 1921, 27A.

[79] *Ber.*, 1919, **52**, 2011; *J.*, 1920, 81A; *J. Chem. Soc.*, 1920, **118**, i., 93.

[80] *Proc. Soc. Exp. Biol. Med.*, 1918, **16**, 25; *Chem. Abs.*, 1919, **13**, 2710; 1920, **14**, 1387 *cf. J.*, 1919, 229R; Sollmann, *J. Pharm. Exp. Ther.*, 1919, **14**, 495; C. Voegtlin and A. E. Livingston, *Chem. Abs.*, 1920, **14**, 1158.

[81] A. M. Hjort and J. T. Eagen, *J. Pharm. Exp. Ther.*, 1919, **14**, 211; *Chem. Abs.*, 1920, **14**, 1161; A D. Hirschfelder, A. Lundholm, and H. Norrgard, *ibid.*, 1920, **15**, 261.

ORGANO-METALLIC COMPOUNDS.

Antimony Compounds.—R. G. Fargher[86] has published a résumé of the present state of our knowledge in the application of organic compounds of antimony in medicine, and points out that only two types seem promising for therapeutic application, viz., the "emetics" (*e.g.*, tartar emetic and its sodium and aniline analogues) which have long been used, and the substituted aminophenylstibinates. Potassium and sodium antimonyl tartrates have been the subject of numerous papers in the medical press during recent years and there are few tropical diseases for which they have not been tried.

An important paper has been published by H. Schmidt[87] dealing with the preparation of arylstibinic acids by the action of diazonium compounds on sodium antimonite. These compounds are shown to be derivatives of polymerised antimonic acids, *e.g.*, phenylstibinic acid HO.SbPh(:O).O.SbPh(O:O).O.SbPh(:O).OH, which under the action of alkali and water yield the alkali salts of monomolecular arylstibinic acids, the latter, however, readily polymerising when liberated.

"Stibacetin" (sodium *p*-acetylaminophenylstibinate), one of the most promising of these substances from the therapeutical point of view,[88] is obtained by the interaction of sodium antimonite and diazotised monoacetyl-*p*-phenylenediamine in alkaline solution: $AcNH.C_6H_4.NH_2 \rightarrow AcNH.C_6H_4.N_2Cl \rightarrow AcNH.C_6H_4.SbO(ONa)OH$.

An interesting paper on the trypanocidal action of antimony compounds has been published by C. Voegtlin and H. W. Smith.[89]

Arsenic Compounds.—The already voluminous literature of "salvarsan" has been extended considerably during the year, especially on the medical side. R. G. Fargher and F. L. Pyman[90] have published a paper on the composition of salvarsan in which they bring out the interesting point that this drug is not, as it has generally been represented to be, pure 3.3′-diamino-4.4′-dihydroxyarsenobenzene dihydrochloride, but contains in addition secondary constituents, which seem to be of considerable importance since when special pains are taken to exclude them the product may be more toxic than when they are present. The retained solvent is shown to be chiefly, if not entirely, water, so that Kober's theory that the variable toxicity of salvarsan is due to retained methyl alcohol is disposed of, the amount of methyl alcohol present varying only from nil to 1·4%. The commercial drug also contains 1–2% of sulphur, partly present in the form of an acid, probably a sulphamic acid $R.NH.SO_3H$, and partly attached to arsenic, whilst some may also be present merely in physical association.

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[82] *J. Amer. Med. Ass.*, 1920, **75**, 566.

[83] D. I. Macht, *Proc. Soc. Biol. Med.*, 1919, **16**, 85; *Chem. Abs.*, 1919, **13**, 2928.

[84] D. I. Macht, *Chem. Abs.*, 1920, **14**, 1367; *cf.* 1919, **13**, 41.

[85] *Pharm. J.*, 1920, **104**, 141.

[86] *J.*, 1920, 333R.

[87] *Annalen*, 1920, **421**, 174; *J.*, 1920, 763A.

[88] Manson-Bahr, *Lancet*, July 24, 1920, p. 178.

[89] *J. Pharm. Exp. Ther.*, 1920, **15**, 453.

[90] *Chem. Soc. Trans.*, 1920, **117**, 370; *J.*, 1920, 111R, 465A; *cf.* C. Strzyzowski, *J. Chem. Soc.*, 1920, **118**, i., 579.

W. G. Christiansen[91] has investigated the preparation of "salvarsan" by the use of hypophosphorous acid as a reducing agent, a process which Fargher and Pyman used for the preparation of "pure" as distinct from "commercial" salvarsan; he finds that the product has a higher average tolerated dose than that prepared by the usual commercial method or by Kober's modifications. The method is stated to be suitable for re-working batches of "salvarsan" too toxic for use, the material being first re-oxidised to 3-amino-4-hydroxyphenylarsinic acid, which is then purified and reduced by hypophosphorous acid to "salvarsan," such reworked "salvarsan" having a tolerated dose of 130–140 mg. per kg.

Z. Klemensiewicz[92] has made determinations of the influence of concentration and mode of preservation as well as of the effect of acids and alkalis on the viscosity of aqueous solutions of "salvarsan."

"Sodium salvarsan," which has been heard of but little in the last two years, is now being made in the United States, as well as in Germany. V. Suzuki[93] has protected a method of preparing this substance.

Favourable clinical reports still continue to be made on "silver salvarsan" in the German medical press.[94] The constitution of this substance has been investigated and discussed by A. Binz, H. Bauer, and A. Hallstein,[95] who have prepared a number of derivatives of the base $As_2[C_6H_3(NH_2).OH]_2,Ag_2O$, the soluble sodium salt of which forms the "silver salvarsan" of commerce. The existence of compounds of "salvarsan" with silver and other

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[91] *J. Amer. Chem. Soc.*, 1920, **42**, 2402; *J.*, 1921, 97A.

[92] *Bull. Soc. Chim.*, 1920, **27**, 820; *J.*, 1920, 801A.

[93] U.S.P. 1,330,288; *J.*, 1920, 281A.

[94] *Ann. Repts.*, 1919, **4**, 501.

[95] *Ber.*, 1920, **53**, 416; *J.*, 1920, 348A; *cf.* A. Binz, *J.*, 1919, 792A.

heavy metals has been known since 1913, and there has been much discussion as to the way in which the metal is attached. These authors show that the silver is not present as a colloid, but occurs as silver oxide in some complex form, and on this and other grounds they are of opinion that Karrer's view[96] that the silver is held by the residual affinities of the arsenic atoms, is untenable and they are inclined to think that it is attached through the amino groups or, as Dilthey has suggested already, to the molecule as a whole and not to any particular group.

H. Schmidt[97] has investigated the preparation of aromatic arsinic acids by the action of sodium arsenite on diazonium solutions, and finds that the most favourable conditions are secured when the solutions are sufficiently alkaline to permit of the reaction represented by the equation $ArN_2Cl + AsO_3HNa_2 = ArAsO_3HNa + NaCl + N_2$. Under such conditions *o*-nitrodiazobenzene gives a yield of phenylarsinic acid equivalent to about 90% of the theoretical but in other cases the quantities of by-products formed are much more considerable. An acid medium is only favourable when strongly acidic constituents are present in the benzene nucleus.

R. G. Fargher[98] utilised this reaction in the preparation of 3-methoxy-4-hydroxy-, 3-hydroxy-4-methoxy-, and 3.4-dimethoxy-phenylarsinic acids which were nitrated and the reduction of the nitro-derivatives investigated. 3-Methoxy-4-hydroxy-5-nitrophenylarsinic acid on reduction gave 3.3′-dimethoxy-4.4′-dihydroxy-5.5′-diaminoarsenobenzene, which closely resembled salvarsan (from which it differs only in the presence of two methoxyl groups) in chemical properties and toxicity. The nitro derivatives of the other two compounds on reduction behaved abnormally and yielded eventually polyarsenides of the types R_2As_4 and R_4As_6 (or R_2As_3) respectively.

A. Mouneyrat[99] has protected a modification of this process for the preparation of aromatic arsinic acids in which arsenious acid in cold or warm, aqueous or dilute alcoholic solutions is caused to react with diazo-compounds in an acid, neutral, or alkaline medium and in presence of two catalysts, one a copper salt and the other a reducing substance, the nature of which varies with the medium in which the operation is carried out, *e.g.*, hypophosphorous acid in acid solution, sodium hydrosulphite in a neutral medium, and so on. A number of examples of the application of the process to phenylarsinic acid are given as well as a list of other aromatic arsinic acids prepared by the process.

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[96] P. Ehrlich and P. Karrer, *Ber.*, 1915, **48**, 1634; Karrer, *Ber.*, 1919, **52**, 2319.

[97] *Annalen*, 1920, **421**, 159; *J.*, 1920, 763A; *cf. J.*, 1913, 1030.

[98] *Chem. Soc. Trans.*, 1920, **117**, 865.

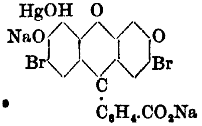
[99] E.P. 142,947; *J.*, 1920, 527A.

Mercury Compounds.—Allusion has been made above to the compounds which "salvarsan" forms with the heavy metals. Of these the copper, silver, and mercury derivatives have already been used, at least experimentally, in medicine. A similar attempt to apply arsenic and mercury in one medicament is that of G. W. Raiziss, J. A. Kolmer, and J. L. Gavron,[100] who prepared and tested pharmacologically an extensive series of mercuriacetates of phenylarsinic acid and its derivatives: these compounds are insoluble in organic solvents, comparatively stable in alkaline solution, though those containing amino groups deposit mercury in presence of alkali. They were not found superior to ordinary organic mercury compounds as germicides *in vitro* and had no greater curative powers in experimental trypanosomiasis: the toxic symptoms produced were those of mercury.

Since mercuridipropionic acid and mercuridibenzoic acid proved to be non-toxic, due to their stability, W. Schoeller, W. Schrauth, and R. Hueter[101] have prepared, with a view to their pharmacological examination, derivatives of a new series of less stable mercuridicarboxylic acids of which methyl sulphidodimercuri-*o*-benzoate $S(Hg{\cdot}C_6H_4{\cdot}CO_2Me)_2$ is a typical example. It is a white powder which at 120° C. is transformed into methyl mercuridi-*o*-benzoate; this in turn is converted by alkalis into mercuridibenzoic acid.

A. Eckmann[102] has patented compounds obtained by the action of one or more molecules of a mercury salt on 1-phenyl-2.3-dimethyl-4-sulphamino-5-pyrazolone, which are stated to possess strong bactericidal and spirillocidal properties.

Two new mercury compounds alleged to combine non-irritant properties with powerful bactericidal action are "mercurichrome" and "mercurophen" (sodium oxymercuri-*o*-nitrophenylate). The former especially has received attention in the medical press of the United States, particularly as a germicide for use in the genito-urinary tract. It is described as a red powder produced by the substitution of one atom of mercury in the molecule of dibromofluorescein and the sodium salt is represented by the following formula (dibromo-oxymercurifluorescein)[103]:



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[100] *J. Biol. Chem.*, 1919, **40**, 533; *J.*, 1920, 134A.

[101] *Ber.*, 1920, **53**, 634.

[102] Schweiz. Serum und Impfinstitut, G.P. 307,893; *J.*, 1919, 28A; U.S.P. 1,347,083; *J.*, 1920, 611A.

[103] H. C. Young, E. C. White, and E. O. Swartz, *J. Amer. Med. Ass.*, 1919, **73**, 1483; *cf.* 1920, **74**, 1224; **75**, 721, 1422; E. C. White, *J. Amer. Chem. Soc.*, 1920, **42**, 2364; *J.*, 1921, 97A.

It was found that a second atom of mercury could be introduced but this did not increase the germicidal action.

Silver Compounds.—So far no true organic compounds of silver have received therapeutical application though many combinations of silver with proteins and organic acids have been used in which the germicidal action of silver is retained without the irritant effects exhibited by inorganic silver compounds. Among new substances of this type mention may be made of A. Lumière's silver sodium thiosalicylate,[104] the readily soluble silver-protein compounds obtained by the addition of carbamide or its derivatives,[105] and the complex silver derivatives of glycine and other amino-acids formed by treating silver oxide or its salts with a solution containing about 5 equivalents of the appropriate amino-acid.[106]

A beginning has, however, apparently been made in the preparation of true organic derivatives of silver by E. Krause and M. Schmitz,[107] who have prepared silver-phenyl silver nitrate $(AgPh)_2,AgNO_3$ by the cautious addition of lead triphenylethyl in dry alcohol to an alcoholic solution of silver nitrate: it is a yellow powder, which decomposes at 100° C. and explodes when heated in a test-tube.

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[104] *Lancet*, Nov. 20, 1920, p. 1074.

[105] Farbenfabr. vorm. F. Bayer u. Co., G.P. 322,756; *J.*, 1920, 765A.

[106] H. R. Napp, E.P. 148,074; *J.*, 1920, 640A.

[107] *Ber.*, 1919, **52**, 2150; *J. Chem. Soc.*, 1920, **118**, i., 198.

PHOTOGRAPHIC MATERIALS AND PROCESSES.

By RAYMOND E. CROWTHER, A.I.C.

THE now famous Sankey judgment[1] on the legality of confiscation of a consignment of pyrogallic acid has been responsible for the appearance, during the past year, of foreign competitive materials of "key" characteristics, on the market in this country. The consumer has temporarily benefited from this competition but the manufacturers who had, under the protection afforded by war conditions, achieved commendable success in the manufacture of products never before made in this country, have been confronted with a set of conditions which, unless radically modified, will undoubtedly strangle their efforts to build up an industry capable of joining in world-wide competition later. Against a country which, previous to the war, enjoyed a virtual monopoly in most of the fine chemicals used in photography and which at present has the advantage of an abnormally low rate of exchange, it could not be rationally expected that anything but disaster would overtake the new home industries under the conditions of open imports. When it is recollected that photographic fine chemicals are in many cases intermediates in the dye manufacturing industry, which has also suffered greatly in consequence of the Sankey judgment, the reason for the very noticeable fall in the amount of British manufactures on the photographic market is not far to seek.

Of the developers, *p*-aminophenol, metol, amidol, and monomet are still being made in this country, and the manufacture of quinol (hydroquinone) has recently been commenced. Some new matter connected with the preparation of pyrogallol[2, 3] and of quinol[4] has been published, and W. J. van Sicklen[5] claims to have prepared metol free from all tendency to cause skin trouble. This important question of skin attack is one which might well be considered by a Research Association; there are undoubtedly other factors to be taken into account than personal idiosyncrasy, and it is probable that a very small amount of some specific impurity, resulting from the method of manufacture, is the cause of the trouble.

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[1] *J.*, 1919, 481R.

[2] Nitritfabrik A.-G., E.P. 140,694; *J.*, 1920, 426A.

[3] J. E. Marsh, E.P. 144,897; *J.*, 1920, 582A.

[4] U.S.P. 1,318,631 and 1,322,580; *J.*, 1920, 9A, 100A.

[5] *Camera Craft*, 1920, **27**, 23.

p-Aminosalicylic acid, under the name of "Neol," has been placed on the market by J. Hauff & Co., who claim that in conjunction with a caustic alkali, it will correct the undesirable effects of gross over-exposure to a greater degree than other rapid developers. The correction is attributed to pronounced tanning powers of the substance formed by reaction with the light product in the film. Lüppo-Cramer, however,[6] expresses doubts both as to any specific corrective action and on the theory propounded. As far as other chemicals are concerned, there has been a marked tendency towards a reduction in prices, more particularly perhaps in the case of bromides. Of the base materials, paper of suitable quality has been more and more difficult to procure. The quality of that most readily procurable leaves much to be desired. Even when well isolated from the emulsion in the process of manufacture, considerable deterioration of the emulsion has been frequently met with. The materials used in the wrapping and the method of packing usually employed in which the face and back of alternate sheets are in contact, are frequently responsible for the failure to "keep" on storing. The deterioration is most apparent when sulphide-toned prints are produced, although in many cases even two or three month's storage effects deterioration which can be observed in ordinary black-and-white developed prints—a state of affairs which only resulted after prolonged storage of pre-war material under indifferent conditions. The recovery of the silver from exhausted fixing baths has been the subject of some discussion in the photographic press,[7] but no suggestion of the use of a salt other than "hypo" as the fixing agent has been forthcoming in order to facilitate the electrolytic recovery of silver in the metallic state. F. F. Renwick[8] has called attention to the practicability of a solution of potassium cyanide for the fixing of gelatin emulsions, and it should be worth while investigating the electrical recovery of the silver from exhausted baths of this salt. As was to be anticipated, the abnormally high price of silver was not long maintained and no work on its replacement by less expensive metals has appeared. The process of photography devised by K. Wilcke,[9] although it employs no light-sensitive silver compound, can scarcely be considered of practical importance. It is of theoretical interest, however, as affording another instance of the application of the characteristic property of selenium of decreasing in its electrical resistance when illuminated. Attempts have been made in the past to utilise this property in the construction of photometers, but without much success. Recent improvements in the manufacture of light-sensitive cells indicate that experimentation with the new materials would give interesting and probably successful results, leading to the construction of an instrument which would entirely eliminate the personal factor.

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[6] *Phot. Korr.*, 1920, **57**, 270.

[7] *Brit. J. Phot.*, 1920, **67**, 351, 499, 563.

[8] *J.*, 1920, 156T.

[9] *Phot. Korr.*, 1920, **57**, 173; *J.*, 1920, 705A.

NEGATIVE PROCESSES.

The properties of gelatin are receiving the attention which the importance of this product demands, and as a result, the chemical rôle of this amphoteric colloid is becoming more and more apparent. D. J. Lloyd,[10] in publishing experimental evidence of the amphoteric nature of gelatin, expresses the opinion that gelatin consists of a solid framework of neutral gelatin (only stable at its iso-electric point, $p_H=4{\cdot}6$ at 20° C.) which is insoluble in cold water, containing some combined water, and an interstitial fluid which is a solution of a gelatin salt.

T. R. Briggs and E. M. C. Hieber[11] have studied the phenomenon of the liquefaction and gelatinisation of gelatin by salts and conclude that the processes are strictly reversible. Lüppo-Cramer[12] offers a satisfactory explanation of some hitherto obscure features of development by reference also to the chemical deportment of gelatin. The idea that gelatin acts only as a protective colloid allowing of the formation of relatively large and sensitive grains or crystals in the preparation of emulsions, and physically inhibiting the action of developing solutions on the unexposed areas of the film, will have to be abandoned in view of the work which has been published during the past year.[13] The physical properties of gelatin cannot be disregarded with impunity, however, and the turbidimeter described by S. E. Sheppard[14] should prove useful in any photographic laboratory.

DEVELOPMENT.

The action of developers on the latent image has been the subject of some considerable amount of study. B. Homolka,[15] continuing his work on the isomerism of developers (in this instance, the polyhydroxybenzoic acids), and taking into consideration the dissociation constants of the hydroxybenzoic acids, concludes, that the failure of gallic and protocatechuic acids to function as developers is attributable to anhydride condensation between the OH group of the carboxylic radicle and the H of the OH situated in the para position. It is pointed out that the anhydride of the former acid can be regarded as a derivative of resorcinol and the latter as a derivative of phenol, neither of which substances functions as a developer. If the disposition of the side-chains or their constitution is such that anhydride condensation yields a derivative of an *o*-dihydroxy compound, or is prevented, developing properties are exhibited. Thus, pyrogallolcarboxylic acid (COOH : OH : OH : OH=1 : 2 : 3 : 4), and the ethyl esters of gallic acid and of protocatechuic acid, will all develop the latent image. The reactivity of the sodium salt of cyclohexane–1.4-diol-1.2.4-trisulphonic acid as a developer[16] is of interest since it necessitates a re-statement of the theory enunciated by Homolka and already referred to.[17] A general survey of the mechanism of development is given in a communication by S. E. Sheppard and G. Meyer[18] who, reasoning by analogy from the proved adsorption of dyes by freshly precipitated silver bromide, conclude that the Lainer effect, *i.e.*, the acceleration of development resulting from the treatment of an exposed plate with dilute potassium iodide solution, and which is chiefly noticed when organic developers of low reduction potential (*e.g.* quinol) are used, is due to increased adsorption and complex formation as between silver halide and developer. A fogging action of dilute potassium iodide solution on silver bromide emulsions is recorded in the same communication and is ascribed to nucleus infection of the grains.

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[10] *Biochem. J.*, 1920, **14**, 147 ; *J.*, 1920, 419A.

[11] *J. Phys. Chem.*, 1920, **24**, 94 ; *J.*, 1920, 274A.

[12] *Phot. Ind.*, 1920, 173.

[13] "Report on industrial applications of colloid chemistry. Dept. of scientific and industrial research." *Brit. J. Phot.*, 1920, **67**, 645.

[14] *J. Ind. Eng. Chem.*, 1920, **12**, 167 ; *J.*, 1920, 282A.

[15] *Phot. Korr.*, 1919, **56**, 387 : *J.*, 1920, 428A.

A. H. Nietz[19] has conducted an enquiry into the development potentials of the organic developers. A new and valuable method of determining these potentials was worked out and the following conclusions were arrived at :—" The effect of bromide on a developer depends upon its reduction potential. If a developer is of low potential, a given amount of bromide will have a larger effect in lowering the density than it will if the developer has a high potential...... Maximum contrast......is not correlated with reduction potential. No definite relation can be shown to exist between the time of appearance and the reduction potential, neither does the fogging power of a developer depend upon its potential." Figures are given which show that the aminophenols are the most energetic, the hydroxyphenols next, and the amines the least. Both nuclear and side-chain (in the amino group) methylation increase the energy. Introduction of a second amino group greatly increases the energy, whilst change to a glycine and the introduction of a -CH_2OH group lower the energy. Evidence was found that fog is practically absent from the high densities and increased as the image density decreased.

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[16] W. Fuchs and B. Elsner, *Ber.*, 1919, **52**, 2281.

[17] *Ann. Repts.*, 1919, **4**, 516.

[18] *Phot. J.*, 1920, **60**, 12 ; *J.*, 1920, 248A.

[19] *Ibid.*, 1920, **60**, 280 ; *J.*, 1921, 62A.

Lüppo-Cramer is responsible for the publication of much valuable matter relative to development reactions. In addition to the explanation of the developing power of aqueous solutions of amidol and similar compounds already referred to[12]—an explanation which assumes reaction of the gelatin with the salt-forming acid of the developing compound, with consequent liberation of the active free base—he has thrown light on the phenomena of "depth" development, and the desensitising action of developing solutions[20]; the study of the latter action has led to the discovery of a practical method of developing even highly colour-sensitive plates by inspection, in bright yellow light.[21] It is only necessary to treat the exposed plate for one minute in the dark with a 1:2000 solution of phenosafranine. The desensitisation effected by such treatment is of such an order that thereafter the plate can be handled without any risk of fog in light sufficiently actinic to fog rapidly wet "slow" bromide paper. The action of the phenosafranine appears to be entirely chemical, since a film of gelatin dyed under the same conditions transmits the entire visible spectrum; any colour-screening action of the dye is thus precluded. Moreover, Lüppo-Cramer has been able to demonstrate that the free amino groups contained in the dye play an important part in the reaction.[22] The marked acceleration of the action of the slower developers resulting from the desensitisation treatment affords further evidence of the chemical nature of the process, as does also the fact that the printing-out sensitiveness is enhanced as the desensitisation to latent image formation becomes more pronounced. Altogether the subject appears to be of great importance both practically and theoretically, and promises to lead to a clearer understanding of the mechanism of sensitisation. The accelerative effect of increasing amounts of sodium sulphite in amidol developing solutions is attributed by Abribat[23] to reciprocal catalytic action of the sulphite in the oxidation of amidol, other oxidation catalysts producing a similar effect. Exactly what proportion of the acceleration caused by the sodium sulphite is attributable to this catalysis is difficult to judge, in view of the fact that increase in the sodium sulphite concentration leads to increase in the basicity of the amidol, a fact which would alone account for most of the observed acceleration. A general review of the organic developers is given by A. Seyewetz,[24] who repeats the statement that the developing properties are raised to a maximum by the introduction of a nuclear methyl group in the ortho position to the hydroxyl group, a statement which does not agree with the results obtained by Nietz[19] who quotes a reduction potential of 7 (quinol=1) for *p*-amino-*o*-cresol and 9 for *p*-amino-*m*-cresol. The tendency of repeatedly used developing solutions to produce dichroic fog has been found by L. Lobel[25] to be due to the accumulation of colloidal silver in the solution. The conditions of low carbonate concentration with high sulphite concentration favour the formation of colloidal silver, and it was found that an addition of 20% sodium sulphate causes flocculation of the silver, which can be readily filtered off. Simultaneous development and fixation of photographic images has been further investigated by A. and L. Lumière and A. Seyewetz.[26] These workers confirm the previous conclusions of C. Otsuki and T. Sudzuki, and suggest a combination of chloranol and caustic alkali, or of metoquinone and tribasic sodium phosphate as practical formulae. The process is particularly recommended for the treatment of over-exposed images. Identification of the products resulting from development reactions appears to be receiving no attention. Workers in this branch of research will be interested in the results of W. Eller and K. Koch[27] who find that the dark brown substances formed by the action of air on phenols, *e.g.*, catechol and quinol, are identical with the humic acids, which are found amongst the decomposition products of vegetable organisms and of certain sugars.

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[20] *Phot. Ind.*, 1920, 505, 664.

[21] *Ibid.*, 1920, 378 ; *Die Photographie*, 1920, No. 10, 1 ; No. 11, 1.

[22] *Der Photograph*, 1920, 337.

[23] *Bull. Soc. Chim.*, 1919, **25**, 569 ; *J.*, 1919, 963A.

PANCHROMATIC AND COLOUR PHOTOGRAPHY.

The theoretical considerations which affect the orthochromatism of the results obtained on "self-screened" orthochromatic plates have been enumerated by Lüppo-Cramer.[28] It is pointed out that by suitable variation of the exposure and development of such plates, it is possible completely to reverse the photographic effects of blues and yellows. Inasmuch as "depth" development give the truest orthochromatic renderings on these plates, efficient anti-halation backing is a *sine qua non* of correct technique. A fair amount of material has been published on the application of the isocyanines and allied dyestuffs as colour-sensitisers, and it is interesting to note that the property of conferring extra sensitiveness on an emulsion has been cited as evidence of chemical constitution.[29] W. J. Pope and W. H. Mills have given an account of their researches on the isocyanines,[30] which result from the alkali hydroxide condensation of quinoline alkiodides with quinaldine alkiodides, and on the carbocyanines,[31] prepared by the condensation of two molecules of a quinaldine alkiodide with one molecule of formaldehyde under the influence of alkalis. The original papers should be consulted for details as to the methods of preparation and examination of the dyes investigated. As far as the sensitising properties of the isocyanines are concerned, the following conclusions may be recorded:—1.1′-Dimethylisocyanine iodide posses powerful sensitising properties, and the maxima for the extra-sensitiveness conferred lie at 5850 and 5350; the positions of these maxima are only slightly affected by the introduction of other methyl groups. The whole spectrograph curve is rendered more uniform by the introduction of a methyl group in the 6-position and the maxima are depressed by introducing a third methyl group in the 6′-position or three methyl groups in the 2′.6.6′-positions. The total induced sensitiveness diminishes steadily as the molecular weight of the dye increases. The substitution of methyl by ethyl leads to a notable diminution in the sensitiveness for red and green light. The diethyl compound (1.1′) is affected similarly to the 1.1′-dimethyl derivative by the introduction of a methyl group into the 6-position or into the 2′-position, indicating a definite relation between the sensitising action and the chemical constitution. The introduction of a cyano or a phenyl radicle into the 2′-position practically annuls the strong sensitising action of the 1.1′-dialkylisocyanine iodide, a fact which, taken in conjunction with the modern views on the interaction of light waves with compounds consisting of two basis groups—one saturated and the other unsaturated—connected by a chain of conjugated ethylenic linkages, leads to the conclusion that all the 2′, 3′, and 4′-substituted isocyanines will prove to be feeble sensitisers.

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[24] *Chim. et Ind.*, 1920, **3**, 28; *Brit. J. Phot.*, 1920, **67**, 186.

[25] *Bull. Soc. Franç. Phot.*, 1920, **7**, 21; *J.*, 1920, 558A.

[26] *Brit. J. Phot.*, 1920, **67**, 747; *J.*, 1921, 28A.

[27] *Ber.*, 1920, **53**, 1469; *J.*, 1920, 717A.

[28] *Phot. Rund.*, 1920, **57**, 129.

In the carbocyanine series, the most important member of which is Sensitol Red (Pinacyanol), the derivatives generally exhibit a decrease in sensitising action as the size of the substituent group increases. It is suggested that the type distinction between the isocyanines and the carbocyanines lies in the coupling of two quinoline residues by the link :CH– in the former case, and by the conjugate chain :CH.CH:CH– in the latter. The multiplication of the number of units of the constitution :CH–, which occurs in the carbocyanine is accompanied by an extension of the extra-sensitisation far into the red region of the spectrum. Although for obvious reasons no variations in the method of applying the dyes to the plate were tried, it would no doubt greatly increase our knowledge of sensitisation mechanism if the opportunity afforded by the possession of what must constitute a unique range of homologous substances, were taken and an investigation in such media as collodion etc. carried out.

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[29] W. H. Mills and others. *Chem. Soc. Trans.*, 1920, **117**, 579, 1035, 1550; *J.*, 1920, 540A, 685A; 1921, 41A.

[30] *Phot. J.*, 1920, **60**, 183; *J.*, 1920, 468A.

[31] *Ibid.*, 253; *J.*, 1920, 802A.

H. Barbier[32] has described the methods of preparation of dimethyl- and diethyl-amino derivatives of the condensation products of quinolines, quinaldines, and lepidines, all of which are stated to be of interest as photographic colour-sensitisers, and L. E. Wise and E. Q. Adams have been granted patents covering Pinaverdol[33] and the 1.1′.2′.6.6′-pentamethyl derivative of isocyanine.[34] The latter compound, however, does not appear to be of outstanding value (*vide* [30]).

The addition of Auramine to the dyes which are generally used for colour-sensitising has been found by F. F. Renwick and O. Bloch[35] to yield improved results by enhancing the sensitiveness in regions not sensitised by the Auramine alone, and by the suppression of the well-known tendency of the isocyanines to produce fog. The action of the Auramine may conceivably be chemically related to that of ammonia, which latter has been studied by S. M. Burka,[36] whose work has demonstrated that the so-called "hypersensitising" does not of necessity lead to the production of fog or to pronounced loss of keeping qualities.

The keeping qualities of even pre-war panchromatic plates have been found by L. T. Woods[37] to be of a very high order, and with the purer dyes which are now available, all modern panchromatic plates should show but very slight deterioration after prolonged storage.

Two hitherto unknown methods of imparting colour-sensitiveness to gelatino-bromide emulsions have been referred to during the past year. J. G. Capstaff and E. R. Bullock[38] have found that treatment of a plate with dilute sodium bisulphite or bicarbonate solution, followed by washing in distilled water, confers marked sensitiveness in regions of the spectrum to which the original emulsion was insensitive, and F. F. Renwick[39] has noticed a similar action of dilute solutions of potassium iodide and cyanide. He suggests that the fogging effect of the former salt, noticed by

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[32] *Bull. Soc. Chim.*, 1920, **27**, 427 ; *J.*, 1920, 528A.
[33] U.S.P. 1,338,346 ; *J.*, 1920, 502A.
[34] U.S.P. 1,338,349 ; *J.*, 1920, 502A.
[35] *Phot. J.*, 1920, **60**, 145 ; *J.*, 1920, 428A.
[36] *J. Franklin Inst.*, 1920, **189**, 24 ; *J.*, 1920, 207A.
[37] *Brit. J. Phot.*, 1920, **67**, 563.
[38] *Ibid.*, 719 ; *J.*, 1920, 834A.
[39] *Phot. J.*, 1921, **61**, 12 ; *J.*, 1921, 99A.

Sheppard and Meyer, and attributed by them to nuclear infection, was the result of such sensitisation and subsequent exposure to the red light of the dark-room. No theoretical explanation of this sensitisation by inorganic salts has been so far offered by Capstaff and Bullock; Renwick,[40] on the other hand, suggests that the treatment with the sensitiser causes an alteration in the dispersive state of the solid solution of colloidal silver which he has previously referred to as the sensitive entity in ripened emulsions (*vide* [8]). It is perhaps noteworthy in this connexion that whereas a dilute solution of potassium iodide (1:5000-1:50000) nduces red-sensitiveness in an unexposed emulsion, stronger solutions (1:100) induce a sensitiveness in the latent image which s confined to the blue end of the spectrum.

Before passing to the year's work in colour photography it may be noted that A. Miethe and E. Stenger[41] have examined spectroscopically several dyes which can be used for the preparation of filters transparent to ultraviolet light, and K. S. Gibson, E. P. T. Tyndall, and H. J. McNicholas[42] have published curves showing the properties of the filters which have been found most useful in the detection of camouflage.

In colour photography the outstanding novelties are perhaps the processes of Katsujiro Kamei and W. V. D. Kelley, both of which are particularly applicable to cinematography. In the former process[43] a suitable arrangement of colour filters and prisms allows of each projected picture being a composite image of two simultaneously recorded colour images and successive pictures exhibit different regions of the spectrum. The sequence of colours is so chosen that not only is the combined effect truer to nature than is generally the case, but also eye irritation is largely eliminated. No attempt is made apparently to adjust the contrast of the colour-sensation negatives to compensate for the variation due to the wave-length of the light recorded on the negative. This variation of gradation due to wave-length differences has been investigated by A. Hnatek,[44] who finds that the curves obtained by plotting gradation against wave-length show in all cases an S-formation, rising from short wave-length up to a maximum for ordinary plates at about 4500$\mu\mu$, falling to a minimum, and then rising again at about 4900$\mu\mu$. Chromatic plates show some variation both as to position and height of the maximum. These results explain many of the seemingly contradictory statements which have been published on this subject.

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[40] *Brit. J. Phot.*, 1920, **67**, 743.

[41] *Z. wiss. Phot.*, 1919, **19**, 57; *J.*, 1920, 313A.

[42] *Brit. J. Phot.*, 1920, **67**, 9.

[43] E.P. 143,579; *Brit. J. Phot.*, *Col. Sup.*, 1920, 27.

[44] *Z. wiss. Phot.*, 1916, **15**, 271; *J.*, 1920, 45A.

W. V. D. Kelley[45] has been granted a patent for a process of colour cinematography in which a double coated positive film is "ruled" by exposure under a symmetrical grating so that the lines on one side correspond with the spaces on the other. By printing on this film from colour-sensation negatives and then toning the images (and rulings) to the complementary colours, a natural coloured additive picture is obtained when the film is viewed by transmission (projection). Provided that in successive pictures the screen pattern does not always occupy identical areas, the process should give excellent results.

The substitution of a blue filter for the green one during a portion of the exposure of the green sensation negative in two-colour cinematography—the more distant the object being photographed the greater is the proportion of the exposure through such blue filter—has been patented by L. F. Douglass[46]; whilst W. V. D. Kelley[47] has patented the expedient of giving an unscreened partial exposure when taking colour-sensation cinematograph negatives. Both these modifications, to carry out which will entail, unfortunately, complications in the apparatus, should lead to more harmonious renderings of the projected images. In additive colour work not primarily intended for cinematography, phenol-formaldehyde condensation products have been recommended as components of the "screen" by M. Wieland[48]; the ability to withstand somewhat rough usage coupled with their insolubility, renders such products eminently suitable for the purpose. The use of fine transparent grains of magnesium carbonate, as proposed by T. Silbermann,[49] does not appear so promising, as very efficient waterproofing protection would have to be applied over the grains in order to prevent their being attacked by the solutions which are used for reversal of the image in non-symmetrical screen-plate colour photography.

It is pointed out by P. R. Kögel[50] that many of the benzopyrilium (anthocyan) compounds occurring in flowers are sufficiently light-sensitive for use in the bleach-out process. *o*-Anethol was found to sensitise several otherwise unsuitable colours of this class, and by reason of its sensitisation to light by thiosinamine it is concluded that Rhodamine S is constitutionally related to cyanidine chloride—a further instance of the application of photosensitiveness in the study of chemical constitution. The same worker[51] has detailed the conditions which it is necessary to observe

[45] U.S.P. 1,337,775 ; *J.*, 1920, 468A.

[46] U.S.P. 1,325,280 ; *J.*, 1920, 136A.

[47] U.S.P. 1,322,794 ; *J.*, 1920, 83A. U.S.P. 1,325,204 ; *J.*, 1920, 136A.

[48] E.P. 137,502 ; *J.*, 1920, 248A.

[49] G.P. 313,008 ; *J.*, 1919, 878A.

[50] *Phot. Korr.*, 1920, **57**, 86 ; *J.*, 1920, 583A.

[51] *Ibid.*, 1919, **56**, 332 ; *J.*, 1920, 427A.

in order to obtain prints in colour by the use of coloured enolic compounds. As the mordant dye process of producing coloured images is likely to become of increasing importance in natural colour positive work, it is of interest to note that F. E. Ives[52] has improved his method of bleach-mordanting the silver image so that a translucent or transparent result may be obtained at will.

POSITIVE PROCESSES AND AFTER-TREATMENTS.

A method of measuring the gloss of photographic printing papers which depends upon the polarisation of reflected light has been described by K. Kieser,[53] and F. Formstecher [54] has modified the well-known crossed-wedge process in such a way as to make it of relatively easy application to the determination of the characteristic curve of printing-out papers. The last named worker has also published [55] the results of his researches on the colour of the images given by printing-out papers. He confirms Chapman-Jones' contention that the colour is a function of the size of the precipitated silver particles and finds that emulsions having a low citric acid content give blue images, whilst redder and softer results are obtained as the proportion of this acid increases. G. Staess [56] proposes to increase the steepness of gradation of the print when using printing-out paper by interposing between the negative and the paper a thin film of gelatin or collodion stained with ferric thiocyanate, the colour of which is bleached inversely in proportion to the opacities of the negative being printed. R. Namias [57] recommends the addition of small amounts of alkali to the sensitising bath used in the carbon process with the object of obtaining papers which exhibit enhanced keeping qualities. Before printing, the alkali is neutralised by fuming the paper in the vapour of a volatile acid, *e.g.*, acetic acid.

A prussiate paper which also exhibits pronounced resistance to deterioration on being stored in the dark, can be prepared, according to E. Bertsch,[58] by the addition of 10—20% of an alkali oxalate to an alkali ferric oxalate before treatment with ferricyanide. The colour of the image changes during printing through various shades of green and blue to a yellowish grey, and on washing it is claimed that pure white lines on an intense blue ground are obtained. The preparation of a duplicating stencil by photographic means has been patented by S. J. Walters.[59]

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[52] *Brit. J. Phot., Col. Sup.*, 1920, 43.

[53] *Z. angew. Chem.*, 1919, **32**, 357 ; *J.*, 1920, 83A.

[54] *Phot. Korr.*, 1920, **57**, 191 ; *J.*, 1920, 640A.

[55] *Deuts. Opt. Woch.*, 1920, 33 ; *J.*, 1920, 640A.

[56] G.P. 316,087 ; *J.*, 1920, 386A.

[57] *Il Progresso F oto.*, 1915, 208 ; *J.*, 1920, 207A.

[58] G.P. 320,891 ; *J.*, 1920, 676A.

[59] U.S.P. 1,327,931 ; *J.*, 1920, 248A.

The process, which is likely to find a fairly wide application provided a composition is used capable of withstanding the "handling" which the inking imposes, is virtually the transference of a carbon print to a support of fine texture through which the duplicating ink will pass when rolled up in the ordinary way.

A most important step in the sphere of practical photography has been made by the introduction of the so-called "dye impression process,"[60] which is the outcome of several years' experimental work by F. W. Donisthorpe. Briefly, the process consists in making a negative on any suitable base—either rigid, pliable, opaque, or transparent—treating this negative with a solution which induces selective absorption of dye, immersing thereafter in a suitable dye solution, and after a brief rinse, transferring the dye image to a gelatin- or baryta-coated support by a short time contact under slight pressure. The transferred print is then rapidly dried to prevent diffusion of the dye with consequent loss of definition in the finer details. Apart from the obvious economy and convenience of such a process, it is evident that since only surface images are necessary, only the under-exposure portion of the characteristic curve of the sensitive negative material need be used and thus an emulsion of ordinary speed (in the H. and D. sense) becomes one of extreme rapidity; the development process is shortened and the positive results exhibit sufficient accuracy of tonal rendering to allow of the process being applied for most work. In addition the range of colours of the positives is practically unlimited, being dependent only on the availability of suitable dyes.

Very little has been published relative to the toning of photographic images, but the papers of R. Namias[61] on combined selenium and sulphur toning, of J. Durbreton[62] on the combination of nickel and cobalt ferricyanides, and of J. M. Blaney[63] who converts the silver image to a tin salt which acts as a mordant for dyes, are worthy of note.

J. W. Pilkington[64] advocates the use of barium sulphide in lieu of "liver" of sulphur in the so-called cold-toning process, which still finds much favour amongst professional photographers. It is claimed by C. Schleussner A.-G.[65] that the brown tones obtained by bleaching a developed print, either before or after fixing, with a solution containing mercuric chloride and potassium bromide and subsequently treating with a hypo bath containing a lead salt, are fast to light. The fastness to other influences is not stated, but previous experience of lead toning processes does not encourage one to place much reliance on the all-round permanance of the toned images.

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[60] *Phot. J.*, 1920, **60**, 119; *J.*, 1920, 313A.

[61] *Il Progressio Fotog.*, 1914; *J.*, 1920, 136A.

[62] *Bull. Soc. Franc. Phot.*, 1916, **6**, 304; *J.*, 1920, 136A.

[63] U.S.P. 1,331,902; *J.*, 1920, 314A.

[64] *Brit. J. Phot.*, 1920, **67**, 14.

[65] G.P. 318,503; *J.*, 1920, 428A.

Process Work.

On behalf of the British Photographic Research Association, R. E. Slade and G. I. Higson[66] have published the results of an investigation on the influence of grain size on the gradation which an emulsion is capable of giving. They conclude that the ideal process emulsion should contain grains of one size only, a fact which, although not unknown amongst emulsion makers, does not appear to have been published hitherto. The production of such an emulsion and its coating on a very thin film should place a power in the hands of some of our scientific workers who are using photography in the investigation of problems relating to the constitution of matter. It is conceivable, for example, that the work on the isotopes of the elements, which F. W. Aston[67] is conducting at Cambridge, might be made quantitative in character and afford valuable experimental evidence of the proportion of the isotopes present in the more complex elements.

J. H. Christensen[68] protects the use of anti-swelling agents similar to those patented by A. J. Agnew, F. F. Renwick, and Ilford, Ltd. (Ann. Repts., 1919, 515), for assisting the selective tanning induced by development. Coupled with suitable developing bases in dilute solution, their action has made possible such a degree of tanning in the developed areas that the undeveloped portions may be washed away and the remaining image used in transfer work. The substitution of dyes for the pigments usually added to the carbon tissue resists used in photogravure has been patented by A. C. Braham,[69] who claims that a finer, sharper screen image is secured as the result of such substitution. The blistering which occurs when transferring the carbon print to its metal support is avoided, according to the patent granted to Rotophot A.-G. für graphische Industrie,[70] by an electrolytic matte etching of the support before transferring the print, and a device for mounting the etched intaglio cylinders used in " Rotogravure " so that centring is automatic and neither rocking nor longitudinal shift results from wear, is the subject of a patent granted to J. P. Bland.[71] The present very satisfactory state of affairs in the application of photography in connexion with catalogue illustration and advertising generally is to be attributed in no small measure to the attention which has been given to the design of half-tone screens. The arrangement of the rulings has a considerable bearing on the quality of the finished illustration, and the complexity of suitable designs is exemplified in the patent granted to W. R. B. Larsen.[72]

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[66] *Phot. J.*, 1919, **59**, 260 ; *J.*, 1920, 135A.

[67] *Nature*, 1920, **105**, 8, 231, 547, 617, 633.

[68] E.P. 135,477 ; *J.*, 1920, 428A.

[69] E.P. 137,108.

[70] G.P. 318,867 ; *J.*, 1920, 428A.

[71] E.P. 131,842.

CINEMATOGRAPHY AND X-RAY WORK.

The efficiency of projection screens used in cinematography has been investigated by C. W. Gamble,[73] who with a fixed condition of illumination obtained the judgment of an audience on an experimental picture. Although no attempts seem to have been made to measure the reflecting power at different angles, the results are of practical value and uphold Nutting's recommendation of a face-etched (sand-blasted) back-silvered mirror. Hydrofluoric acid etching was found markedly to restrict the angle of high efficiency. For the projection of subjects exhibiting strong contrasts the placing of a neutral tinted glass screen of low optical density in front of the projection lens is advised as tending to give better tonal quality in the picture. Up to the present celluloid has not been displaced to any great extent as a cinematograph film base—a fact which is somewhat remarkable, for in spite of its general suitability by virtue of its flexibility, transparency, and durability, the fire risk with celluloid is objectionably high. The substitution of other esters of cellulose is being slowly effected, and the experience gained during the war in the manufacture of non-inflammable dopes should assist in the production of an efficient substitute for celluloid, although the qualifying properties are not the same for dope as for cinematograph film. Ability to withstand a relatively high temperature without disintegration is demanded for the latter purpose if the undesirable complication of apparatus which is at present necessary for the interposition of stationary pictures is to be avoided. It is to be regretted that but little attention is apparently being given to this matter, the only communication of any note bearing thereon during the past year being the patent of W. J. Stevenson,[74] which protects the addition to cellulose acetate of triacetin and triphenyl phosphate in about equal parts and in amount varying between 10 and 20%. Benzyl chloride and tetrachloroethane are stated to be suitable solvents.

The Royal Photographic Society is to be congratulated upon its foresight in assisting in the formation of a technical and scientific section. Amongst its various activities, this section has arranged special meetings for the discussion of the latest advances in photographic science. At a joint meeting of this section and the Röntgen Society many matters of import in radiography were discussed.[75] The Presidential address to the Royal Photographic Society by G. H. Rodman[76] also constitutes a communication of importance to those interested in radiography, dealing, as it did, very fully with the evolution of the X-ray tube. As far as sensitive materials suitable for radiography are concerned, there seems to have been little attention paid to the actual increase of the sensitiveness to X-rays, the majority of workers concerning themselves in perfecting the process in which an intensifying screen is placed in contact with the sensitive surface during exposure. The success so far attained in this direction is gratifying; indeed the results which it has been possible to produce by the use of two intensifying screens—one on either side of a film coated on both sides with emulsion—lead one to anticipate with confidence that perfect radiographs of any part of the human body will be readily secured by instantaneous exposures. The appearance of this so-called "duplitized" film marks the beginning of an epoch which will reveal in the near future a process in which the X-ray sensitiveness of the emulsion will be entirely ignored and the screen excitation be exclusively used to produce the latent image.

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[72] E.P. 129,266.

[73] *Brit. J. Phot.*, 1920, **67**, 553.

[74] E.P. 138,379; *J.*, 1920, 281A

The factors which enter into the practice of radiography with intensifying screens are considered in a communication by R. Wilsey,[77] from which it appears that the form of cassette in which the film is enclosed during the exposure has a considerable influence on the rendering of fine detail. It will be evident that the use of two intensifying screens will in some measure reduce the objectionable grain which frequently mars the detail when one screen only is employed, but a device has been protected by Siemens und Halske A.-G.[78] which should practically eliminate such grain. A continuous metal screen is employed, and it is claimed that the characteristic radiation of the metal excited by the X-rays is most efficient in the formation of a latent image.

SENSITOMETRY ETC.

Perhaps the outstanding event in this section during the year was the publication of the collected papers of Hurter and Driffield, the most important of which were communicated originally to this Society. The value of the publication is materially enhanced by the inclusion of a very complete bibliography of work which has any bearing on the matter dealt with by Hurter and Driffield, and photographic workers throughout the world will appreciate the large amount of painstaking labour which W. B. Ferguson has expended in compiling the volume.

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[75] *Phot. J.*, 1920, **60**, 57.

[76] *Ibid.*, 311.

[77] *Brit. J. Phot.*, 1920, **67**, 285.

[78] E.P. 143,261; *J.*, 1920, 834A.

The question whether in sensitometric work the light intensity factor should be a constant and the time factor a variable, or *vice versâ*, has been but little discussed in the past, it having been generally assumed that the results obtained by either method were reliable. The work of H. J. Channon[79] makes it clear, however, that under certain conditions of low light intensity, the time factor is relatively insignificant.

The intermittence error introduced when instruments of the sector wheel type are used has long been recognised and various attempts have been made to design practical non-intermittent sensitometers. L. A. Jones[80] has described an apparatus of this type which gives results of precision: the measurements made with its aid indicate that both the speed and gamma of a plate are independent of the absolute exposure, not variable with it as is the case when intermittent exposures are investigated. A non-intermittent apparatus of a simpler design, in use in the laboratories of the British Photographic Research Association, has also been described by G. I. Higson.[81] Of the varying density scale sensitometers the Chapman-Jones "test plate" has been perhaps the most generally useful for approximate work hitherto available. A somewhat similar piece of apparatus has been put on the market by J. M. Eder who, in describing its characteristics and the method of applying it in sensitometry, photometry, etc.,[82] compares it with other apparatus much favoured by continental experimenters. Lüppo-Cramer,[83] in reviewing the instrument, points out that the "threshold value" for the determination of which sensitometers of this type are specially designed, is liable to be very misleading as an indication of the usefulness of a sensitive emulsion.

A contribution to the theory of tone reproduction has been made by L. A. Jones,[84] who brings together all previous work on this subject and, after compiling a vocabulary of suitable terms and units, suggests a graphical method of solving the problems connected with the reproduction of tones by photographic processes. The question of the relationship of grain size to sensitiveness has been carefully investigated by T. Svedberg[85] who, working with very thinly coated plates, shows that the curve obtained by plotting exposure against the number of grains made developable thereby is similar to the usual characteristic curve, and that the curve which results from plotting grain size against the number of grains made developable, is an exponential. All his results support the view that the larger grains are the more sensitive. It remains now to be settled whether the sensitiveness of the grain is a function of its size as such or whether the higher sensitiveness of the larger grains arises primarily, if not exclusively, from some other modification of the grain induced by treatment which simultaneously causes growth of the crystals. It seems probable, in view of the very recent introduction of exceedingly fast plates exhibiting low "graininess" which are prepared by a new ripening process, that grain size *ipso facto* and sensitiveness are not necessarily interdependent. Whilst dealing with the subject of grain, reference should be made to the important piece of research which has been conducted by L. A. Jones and N. Deisch[86] on the "graininess" of photographic deposits. The term "graininess" is applied to the characteristic which the practical photographer has hitherto referred to as "grain," and since much confusion has arisen in the past from the application of the latter term to both the original crystals in an emulsion and the aggregates or clumps of reduced silver in a developed image, it is high time that distinctive terms be adopted. Many factors which were reputed to influence graininess were examined quantitatively by means of novel and carefully standardised methods and the results, which are of too varied a character to detail in a report of this nature, are of supreme interest to the "process" worker and the scientist who employs photography in work where images exhibiting maximum resolution are desirable.

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[79] *Phot. J.*, 1920, **60**, 164 ; *J.*, 1920, 468A.

[80] *Ibid.*, 80 ; *J.*, 1920, 313A.

[81] *Ibid.*, 235.

[82] *Phot. Korr.*, 1919, **56**, 244 ; 1920, **57**, 1, 41, 83 ; *J.*, 1920, 803A.

[83] *Phot. Rund.*, 1920, **57**, 193.

[84] *J. Franklin Inst.*, 1920, **190**, 39 ; *J.*, 1920, 676A.

[85] *Z. wiss. Phot.*, 1920, **20**, 36 ; *J.*, 1920, 705A.

The Hurter Memorial Lecture delivered before the Liverpool Section of this Society by F. F. Renwich (*vide*[8]) constitutes one of the most important items in the year's progress, not only on account of the fact that a new unifying theory of the latent image was advanced. In addition an account of the novel experiments, the results of which support this theory, was presented, and a very full bibliography of work on the latent image bears testimony to the large amount of work which has been carried out in the pursuit of this elusive entity.

The above communication, like that of H. J. Channon,[79] in which several more or less uncommon properties of the latent image are dealt with, cannot profitably be dissected for detailed discussion in this report, but their importance will be realised immediately they are consulted in the originals.

It may be noted with satisfaction that the experience in aerial surveying which was gained in the late war is likely to be turned to good account not only in mapping out inaccessible land areas but also in the charting of shoals and hidden reefs under the sea. A communication by W. T. Lee[87] deals especially with this latter work and indicates that valuable information has already been secured.

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[86] *Brit. J. Phot.*, 1920, **67**, 689, 706; *J.*, 1920, 834A.

Before concluding this report—which by reason of the manifold applications of photography in the arts and sciences must of necessity appear somewhat disconnected—reference should be made to the activities of the British Photographic Research Association which appears, judging from the matter which has been published under its aegis,[88, 89, 90] to be getting to grips with the important theoretical problems connected with photography. The breadth of outlook indicated in the above communications inspires confidence that the association will fully justify its existence and augurs well for the future of the photographic industry in this country.

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[87] *Geographical Review*, **10**, [5].
[88] *Phot. J.*, 1920, **60**, 161.
[89] *Proc. Roy. Soc.*, 1920, **A 97**, 181.
[90] *Ibid.*, **A 98**, 154; *J.*, 1921, 27A.

EXPLOSIVES.

By William Rintoul, O.B.E., F.I.C.

During the year 1920 little of an outstanding nature was published regarding military explosives, and we may safely assume that the advances made by the different nations during the war have now been recorded. If any new discoveries have been made by any of the Powers and are not already published, it is probable that these will be retained as official secrets, at least for some considerable time.

A very important address was delivered before the Chemical Society by Sir Robert Robertson on December 16th, 1920.[1] The greater part of this lecture was devoted to a discussion of the influence of the constitution and physical condition of explosives on the heat of formation, the heat of explosion, and gases evolved, chemical stability, sensitiveness to shock, rate of detonation, and pressure developed. Figures were given for the heats of explosion of various substances compared with the heat evolved by the combustion of the equivalent quantities of their constituent elements, the latter figure always being the greater, owing to the heat absorbed in the formation of the explosive. It was also shown that, with similar substances, a lower heat of formation was accompanied by lower chemical stability and increased sensitiveness to impact. It was pointed out that the heat of formation of explosives is of fundamental importance in affording data for the study of their chemical characteristics and the evaluation of their explosive properties. In the section of the lecture devoted to heats of explosion, important advances in the calorimetry of high explosives were recorded. It has been found possible to devise apparatus capable of withstanding the shock of detonating explosives packed to unit density, and the heats of detonation of typical explosives when fired at a density of 1·3 are given.

In dealing with chemical stability the author specifies the factors which govern this property and gives the temperature coefficients of the more important explosives determined over wide limits. A very interesting table of comparative rates of decomposition of various explosives at a uniform temperature is given, from which many important generalisations on the influence of structure on chemical stability can be drawn. The influence of the physical state of the substance on this property is also shown to be important.

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[1] *Chem. Soc. Trans.*, 1921, **119**, 1; *cf.*, *J.* 1921, 26R.

Advances in the design of apparatus for the determination of sensitiveness to shock are referred to. In discussing the influence of constitution on this factor it is pointed out that the higher the heat of explosion the less is the quantity of energy that need be added to bring about detonation. For example, in the case of nitro-compounds it is found that those are the more sensitive which have the lowest heat of formation. It is suggested that velocity of detonation runs in line with the heat of explosion and that it is therefore dependent, to a large extent, on molecular structure.

Perhaps the most interesting part of this important communication deals with the application of Hopkinson's method[2] for the determination of the violence of the blow produced by the detonation of an explosive. This method has been developed and extensively used at the Research Dept., Woolwich, and has given most useful results in connexion with the testing and design of detonator fusees and gaines. Briefly, the test consists in firing the explosive against the end of a fairly long steel bar, at the other end of which there is a small loose section of the same bar. The latter is termed the time piece. The compression wave travels along the bar and is reflected from the end of the time piece, but the juncture between the bar and the time piece is incapable of transmitting a tension wave. Hence the time piece is projected from the end of the bar and the energy of its projection can be measured in a ballistic pendulum. The velocity of the propagation of the explosive wave through the steel is known, so that the mean pressure exerted during an interval of time—depending on the length of the time piece—can be determined. By measuring the total displacement of bar and time piece a value for the total blow can be arrived at. A table of results of this test is given showing the pressure in tons per sq. in. developed by various explosives in $0{\cdot}5 \times 10^{-5}$ seconds for different densities of loading and conditions of confinement. In the case of simple explosives the results appear to be dependent on the rate of detonation, the heat of explosion, the volume of gas produced, and the density of loading, but further data under standard conditions are required before the effects due to each of these can be ascertained.

In the concluding part of his paper Sir Robert Robertson deals with the explosive properties of the "amatols." Both 80 : 20 amatol, containing 80 parts of ammonium nitrate to 20 parts of T.N.T., and 40 : 60 amatol, containing 40 and 60% of these ingredients respectively, are discussed from the point of view of the heats of formation and explosion and of the gases evolved. It is stated that pure ammonium nitrate and T.N.T. have little action on one another, even at a temperature of 120° C., but that certain impurities must be guarded against, as liable to produce either an evolution of gas or chemical interaction, both of which are objectionable. For example, the isomers of T.N.T. which accompany the symmetrical variety would give rise to a somewhat greater evolution with pure ammonium nitrate, but the presence of pyridine as an impurity in the ammonium nitrate is much more objectionable, as it causes tumultuous evolution of gas, even in the cold, with isomers of T.N.T., although not with the symmetrical compound.

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[2] *Phil. Trans. Roy. Soc.*, 1914, pp. 213-437.

The amatols are shown to be relatively insensitive both to impact and to friction. Figures are given for the velocity of detonation of these explosives and for the pressure developed when tested by Hopkinson's method already described.

High Explosives for Military Purposes.

Picric Acid.

A series of experiments have been carried out by M. Marqueyrol[3] on the influence of sulphonation on the yield of picric acid from phenol, the general conclusion being that the yield depends on the relative amounts of mono- and di-sulphonic acid in the sulphonation product, the greater the amount of disulphonic acid the higher the yield. Maximum amounts of disulphonic acid can be obtained by using 93% sulphuric acid and allowing the reaction to proceed at 100° C. for 30 min. to 1 hour. On sulphonating phenol with ten parts of 20% oleum a mixture of di- and tri-sulphonic acids containing more than 80% of the latter is produced. On nitrating this a yield of 90% of the theoretical amount of picric acid is obtained. Apparently the greater the number of sulphonic groups the stronger is the resistance of the phenol to oxidation. These results have been borne out by the work of M. M. Doll.[4] The use of phenol-disulphonic acid for the manufacture of picric acid was practised in Germany during the war, with the further advantage that the nitration could be carried out in ordinary cast-iron vessels.[5] This explosive, the use of which had practically lapsed in time of peace, was, owing to toluene shortage, re-introduced and used principally as an element in the igniting train in shells.[6] R. L. Datta[7] proposes to prepare picric acid by nitrating phenolsulphonic acid with oxides of nitrogen. With a view to overcoming the oxidation by nitric acid in the various forms of nitration, it has been suggested by

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[3] *Bull. Soc. Chim.*, 1920, 27, 140, 143, 190, 199 ; *J.*, 1920, 248A, 249A, 350A.

[4] *Ibid.*, 370 ; *J.*, 1920, 502A.

[5] Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, 148.

[6] G. Gallo, *Giorn. Chim. Ind. Appl.*, 1920, 2, 634.

[7] U.S.P. 1,292,266 ; *J.*, 1919, 305A.

L. W. Andrews[8] to employ an acid amide such as urea dissolved in the nitrating mixture. O. Silberrad,[9] previous to nitration of phenol, forms the *p*-nitroso derivative and thus obtains an improved yield of picric acid.

The method outlined in last year's report for the conversion of dinitrophenol into picric acid is described in A. G. Green's patent.[10] In this method the successive stages are :—Benzene → chlorobenzene → dinitrochlorobenzene → dinitrophenol → picric acid.

An interesting contribution to the catalytic production of picric acid from benzene is that of L. Vignon.[11] It is stated that when 100 parts of the benzene is treated with 800 parts of nitric acid of 36° B. and 20 parts of mercuric nitrate, 138 parts of picric acid and 32 parts of nitrobenzene are obtained. By keeping the benzene in excess, however, using 1000 parts of nitric acid 33°–36° B., 25 of mercuric nitrate, and 500 of benzene, 1150–1250 parts of a mixture containing 52% of dinitrophenol and 48% of picric acid is produced. This resultant mixture may be used directly as an explosive, or converted entirely into picric acid by further nitration.

Trinitrotoluene.

In a paper on the manufacture by a continuous method, reference is made[12] to the Weiler-ter Meer; Meister, Lucius, u. Brüning and the Kubierschky apparatus. The last-named is considered the most rational of the three and marks a real advance in the design of nitration plant. A plant has been patented by H. N. Morris,[13] which consists of a number of superposed reaction chambers each divided into an upper and lower compartment, with communications between them. The upper compartments are fitted with atomisers through which the substances are introduced and the lower with coils to control temperature.

As a means of working up petroleum oils containing aromatic hydrocarbons, E. A. Barnes[14] proposes to nitrate the oil directly with mixed acid. In this way the charge, after nitration, separates into three layers, the top layer being paraffins, the intermediate layer nitro-compounds, and the bottom layer waste acid. The middle layer may then be rectified and further nitrated. E. Berl and F. Ziffer[15] state that on treating Galician and Roumanian oils with liquid sulphur dioxide at -20° C. the products obtained contained benzene, toluene, xylenes, naphthenes, and a certain quantity of aliphatic hydrocarbons. This product was distilled and a fraction of sp. gr. 0·85–0·86 containing 70% of aromatic and 30% of aliphatic hydrocarbons obtained. After elimination of the olefines by washing with sulphuric acid the product was nitrated successfully to mononitrotoluene. The latter was rectified and used for making T.N.T.

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[8] U.S.P. 1,283,617 ; *J.*, 1919, 69A.

[9] E.P. 140,955 ; *J.*, 1920, 398A.

[10] E.P. 16,607, 1915 ; *J.*, 1919, 389A.

[11] *Bull. Soc. Chim.*, 1920, **27**, 547 ; *J.*, 1920, 567A.

[12] *Die Seife*, 1919, **3**, 609.

[13] E.P. 139,234 ; *J.*, 1920, 291A.

[14] U.S.P. 1,273,568 ; *J.*, 1918, 638A.

[15] *Petroleum*, 1919, **14**, 1213 ; *J.*, 1920, 84A.

As a general scheme for the manufacture of T.N.T. with the minimum acid consumption and the best yield, R. Pollitzer and V. Jelocnik[16] propose the following:—The requisite quantity of waste acid from the trinitration is strengthened with nitric acid and used for dinitration; the requisite quantity of waste acid from dinitration is strengthened for mononitration. After completing the mononitration the surplus waste acids from the other two stages are added, mixed together, a proportion of water added and the whole left to settle. In the way this waste acid contains only 0·5% nitric acid and is free from nitro-compounds.

As a means of removing suspended T.N.T. crystals from waste acid, F. M. G. Johnson[17] proposes to place the settling vessel under suction. In this way gases liberated from the waste acid fasten as globules on to the small crystals of T.N.T. and carry them to the surface.

In time of peace the T.N.T. was purified by crystallising from alcohol or toluol; the solvent retains the impurities which are known as liquid T.N.T. and are used for the preparing of mining explosives, and in wartime as an ingredient in the filling of hand grenades. In Germany during the war[18] only a portion of the T.N.T. was crystallised, the pure material being used for specific purposes such as an initiating portion of a detonating train. In some instances for the preparation of high grade T.N.T. the mononitrotoluene was distilled and the ortho- and para-constituents nitrated to give a material of satisfactory purity without recourse to crystallisation.

As having a possible bearing on explosions occurring in the manufacture of T.N.T., A. S. Eastman[19] has shown that in the nitration of bi-oil to T.N.T., the proportion of carbon monoxide in the gases liberated by oxidation may be so high that under certain conditions the mixture of air and carbon monoxide becomes explosive, and this may account for explosions where the top of the nitrator has been blown off without explosion of the T.N.T. In a similar connexion S. Brown[20] has shown conclusively that the action of lubricating oil on a nitration mixture is to accelerate the rate of decomposition of the nitro compound and may accordingly be a source of grave danger.

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[16] G.P. 299,661; *J.*, 1920, 677**A**.

[17] U.S.P. 1,271,578; *J.*, 1918, 608**A**.

[18] G. Gallo, *loc. cit.*

[19] *J. Ind. Eng. Chem.*, 1919, **11**, 1124; *J.*, 1920, 83**A**.

[20] *Chem. Trade J.*, 1920, **67**, 673; *J.*, 1921, 28**A**.

Laboratory tests by W. J. Huff[21] have shown that T.N.T. is practically non-hygroscopic, and A. W. C. Menzies[22] has outlined a method by which its vapour tension at 82°–102° C. has been determined by the aid of a single McLeod gauge.

R. C. Farmer[23] describes an apparatus for the determination of the stability of high explosives by the velocity of gas evolution in a vacuum. All explosives appear to be liable to a gradual decomposition at temperatures considerably below their ignition points. The velocity is greatly affected by temperature and by the catalytic action of impurities. Trinitrotoluene and the isomerides which accompany it do not differ greatly in stability when purified.

A description of the method of loading T.N.T. into shells has appeared[24]; the following methods are detailed :—(1) Melting and pouring direct; (2) pouring shaped charges into one or more blocks and fitting into shells; (3) pressing block charges and fitting into shells; (4) stemming, and (5) pressing direct by hydraulic presses. Cavitation in melted and poured T.N.T. charges on solidification can be prevented by pouring at a temperature as near as possible to solidifying point without allowing the mass to get treacley.

Trinitro-anisole.

Owing to scarcity of toluene the Germans were obliged to employ substitutes for T.N.T. and one of the most largely employed was trinitro-anisole[25] which has the convenient melting point of 62° C. This material was prepared by the action of methyl alcohol and alkali on dinitrochlorobenzene, the resultant dinitro-anisole being then nitrated to the tri-stage. The product is rather more sensitive to shock than T.N.T., has greater fragmentation than the latter, but possesses undesirable physiological properties, and its use was limited to heavy shells.

Hexanitrodiphenylamine.

In the beginning of 1915 hexanitrodiphenylamine was employed by the Germans in torpedoes on account of its high shattering effect, and afterwards in shells of all kinds. On account of its inconveniently high melting point it was sometimes employed mixed with 30–40% of dinitrotoluene,[26] the mixture forming a readily fusible product which sets to a sp. gr. of 1·64-1·70 and detonates with extraordinary violence, forming a most effective charge for torpedoes.

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[21] *Chem. and Met. Eng.*, 1919, **21**, 570; *J.*, 1920, 136A.

[22] *J. Amer. Chem. Soc.*, 1920, **42**, 2218.

[23] *Chem. Soc. Trans.*, 1920, **117**, 1432; *J.*, 1921, 63A.

[24] *Chem. Age*, 1919, 385.

[25] G. Gallo, *loc. cit.*

[26] G. Gallo, *loc. cit.*

J. Marshall[27] proposes a method of preparing hexanitrodiphenylamine by nitrating dinitrodiphenylamine to the tetra-stage, the product thus obtained being separated by filtration and then nitrated to the final stage. This method introduces the use of mixed acid for nitration to the tetra-stage, a procedure which had not hitherto been regarded as possible.

The du Pont Co.[28] has perfected a method of preparation using dinitrochlorobenzene and aniline as raw materials.

Hexanitrodiphenyl Sulphide.

This material has been used largely as a bomb filling, particularly for aeroplane bombs[29]; it is prepared by nitrating chlorobenzene to the trinitro-compound and treating this with sodium thiosulphate in presence of magnesium carbonate and alcohol. The sulphoxide[30] has also been employed as a bomb filling and is particularly effective in view of the suffocating nature of the fumes from it.

Tetryl and Tetranitroaniline.

Tetryl, besides being used as portion of the detonating train in a shell, has been used admixed with T.N.T. as a filling for mines, torpedoes, etc.[31]

A method of preparation of tetryl has been employed by D. H. Wride[32] in which dimethylaniline dissolved in ten parts of sulphuric acid is run into mixed acid containing 72% of nitric acid. The final temperature of nitration is 60° C., and on cooling the tetryl separates out and is purified by dissolving in acetone and precipitating with water. Treatment of waste acid for decomposition of the nitro-compounds is described.

Tetryl readily forms equimolecular additive compounds with the simpler amines,[33] which in many cases readily condense to form picrylamines. The presence of alkyl substituents in the *ortho*-position in the amine does not affect the formation of the additive compound, but inhibits condensation. Naphthylamines and secondary amines form stable addition compounds which do not pass into condensation derivatives.

[27] U.S.P. 1,326,947; *J.*, 1920, 249A.

[28] *U.S. Naval Proc.*, Oct., 1920.

[29] G. Gallo, *loc. cit.*

[30] A. Stettbacher, *Z. ges Schiess- u. Sprengstoffw.*, 1920, 148.

[31] A. Stettbacher, *loc. cit.*

[32] *Arms and Explosives*, 1920, 6.

[33] T. C. James and others, *Chem. Soc. Trans.*, 1920, **117**, 1273.

Investigations by C. L. Knowles[34] at the Eastern Laboratory of the du Pont Co. show that the instability of ordinary tetryl is due, to a large extent, to the presence of tetranitrophenylmethylnitroamine formed by the nitration of methylaniline present in the raw material. It may be removed by boiling with water or with sodium carbonate, soluble trinitromethylnitroaminophenol or its sodium derivatives being formed. Tetryl itself is hydrolysed to a slight extent by sodium carbonate to sodium picrate. The Obermüller test *in vacuo* shows the true stability of tetryl to be indicated by its melting point.

The determination of the critical solution temperature in anhydrous alcohol has been used as a method for identifying as tetryl a product found in an unexploded shell.[35] This method has been extended to other nitro compounds.

In an investigation of the gas evolution from crystalline substances when heated below their melting point, among which tetranitroaniline was investigated, Henselwood[36] has shown that the change appears to be confined to those molecules in the neighbourhood of the surface. Where a progressive disintegration of the crystal structure takes place, the change is strongly accelerated. Solution in another solid causes a reduction in the rate of reaction.

Miscellaneous Explosives.

J. Marshall has outlined a process for preparing trinitroxylene from commercial xylene containing the mixed isomers. Coke-oven by-product xylene gave a more satisfactory trinitro compound than xylene with an identical boiling range from other sources such as water-gas tar or drip oil. No satisfactory explanation of this phenomenon was discovered.[37] In America cast mixtures of trinitroxylene and T.N.T. were developed which could be detonated with smaller boosters of tetryl than were required for refined T.N.T It is suggested that parazole may be extensively made in the future in America.[38]

A process for the production of trinitrocresol has been described by D. H. Wride,[39] in which a yield of 112 parts of Cresylite per 100 parts of cresol employed is obtained.

Dinitrobenzol was extensively employed by the Germans when it was found that it could be detonated by a priming charge of

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[34] *J. Ind. Eng. Chem.*, 1920, **12**, 246 ; *J.*, 1920, 428A.

[35] *Bull. Soc. Chim. Belg.*, 1920, 28, 34.

[36] *Phil. Mag.*, 1920, 569.

[37] *J. Ind. Eng. Chem.*, 1920, **12**, 248 ; *J.*, 1920, 428A.

[38] Wright, *U.S. Naval Inst. Proc.*, 1920.

[39] *Arms and Explosives*, 1920, 47.

T.N.T.[40] The French[41] used a mixture of nitric oxide and nitrobenzol or carbon bisulphide as a shell filling.

Principally owing to a shortage of raw materials, ammonium nitrate found an extensive use as a high explosive in combination with nitro-compounds, chiefly T.N.T.; the explosives made with the latter compound were the ammonals and amatols. In Germany the amatols were used as a shell filling, while for submerged mines a mixture of ammonium nitrate and dinitrobenzene or trinitroanisole was used.

In France, trinitronaphthalene (naphtite) mixed with ammonium nitrate was employed under the name "Scheiderite," while in Germany a similar high explosive was made, using, besides naphtite, trinitroxylenes and nitrated solvent naphtha. The explosive Donarite, which was used in Germany for hand grenades, has the composition: ammonium nitrate 80%, nitro-compound 18%, and woodmeal 2%.

It is stated that amatol is more powerful than T.N.T., but its velocity of detonation and density are lower, so that its shattering effect is not so good. It is not so easy to detonate as T.N.T. and gets more difficult and more inert with increase in ammonium nitrate content. The amatols vary in composition and are made by the following methods:—(1) Milling in any form of mill for any grade of amatol (usually 80 : 20), (2) melting and pouring (40 : 60 and 50 : 50), and (3) hot mix (60 : 40 or 80 : 20).[42]

When the percentage of ammonium nitrate is unduly increased the mass becomes too stiff to pour into shells, and it has been found[43] that addition of sodium acetate, dicyanodiamide, aniline oxalate, or sodium nitrate lowers the melting point of ammonium nitrate to 100° C., so that it can be employed in a high percentage admixed with T.N.T.

The composition of the ammonal employed by the Germans was[44]:—ammonium nitrate 72%, T.N.T. 16%, aluminium powder 12%, the material being compressed into shells at a pressure of 2000 kg. per sq. cm.[45] In some instances trinitronaphthalene was substituted for T.N.T.

Owing to the enormous consumption in Germany of ammonium nitrate it was imperative to seek supplementary oxygen-bearing substances. By the employment of liquid air for mining purposes a large proportion of chlorates and perchlorates could be released for military purposes, and owing to the fact that chlorates are not sufficiently resistant to shock, preference was given to perchlorates.

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[40] G. Gallo, *loc. cit.*

[41] A. Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, 148.

[42] *Chem. Age*, 1919, 408.

[43] Gallo, *loc. cit.*

[44] Gallo, *loc. cit.*

[45] Gallo, *loc. cit.*

One permanent effect of the experience gained by the war has been the retention of sodium nitrate as an ingredient of explosives in place of the more expensive potassium nitrate. It was thought formerly that the use of the sodium salt would entail greater disadvantages than would be compensated by the reduction in cost. The actual practical experience has shown that this is not the case, and a material gain in economy can be effected without incurring any really serious disadvantages.

Chlorates and perchlorates have not regained their pre-war positions as ingredients of explosives, as their cost is still too great to justify their use. The same applies to ammonium oxalate as a cooling agent in safety explosives.

One of the post-war problems which received a good deal of attention was the utilisation of the enormous stocks of cordite and similar explosives which remained in hand at the conclusion of hostilities. Many attempts were made to treat these in such a way as would make them suitable for use as ingredients in blasting explosives, but when the difficulties which arise daily in the use of explosives prepared from fresh materials are considered, it is not surprising that the proposal to introduce an ingredient of such low sensitiveness as cordite was unsuccessful. The cost of the preparation of the cordite in a suitable mechanical condition was another serious drawback.

Nitroglycerin.

An interesting paper has been contributed by F. Hofwimmer[57] on the manufacture of nitroglycerin; the first portions of this paper have already been noted.[58] In the concluding section a modification of the manufacture is discussed, according to which acid nitroglycerin, as it separates from the waste acid, is run into sodium carbonate solution instead of into water. The drowning liquid is kept slightly alkaline, with the result that the solubility of the di- and trinitroglycerin in the washing liquors is materially reduced and the ultimate yield of nitroglycerin is increased. Details are given of a four months' run with the modified process which resulted in an average yield of 230·7% being obtained from fermentation glycerin under conditions which were not particularly favourable. Acid of regular and correct composition would have enabled the yields to be increased by 2–3%, while glycerin from fat would have given 4–5% higher yields. The author concludes that a yield of 236–237% may be expected under reasonably good conditions. The final product contains a larger percentage of dinitroglycerin than by the old process, and this is claimed to be rather an advantage, as it tends to lower the freezing point of the explosive. No difference in heat test was introduced by the modification. It is claimed that the life of the plant is greatly increased and that the economy of time and compressed air is 30–40% and of water 60–80% of that formerly used.

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[57] *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 393; *J.*, 1919, **468A**.

[58] *Ann. Repts.*, 1919, **4**, 536.

Koehler, Marqueyrol, and Jovinet[59] describe the application of Devarda's method to the estimation of nitrogen in nitroglycerin. A quantity of about 0·5 g. of nitroglycerin is mixed with 40 c.c. of hydrogen peroxide (12 vols.) and 5 c.c. of potassium hydroxide solution in a conical flask, and the mixture is heated at 40° C. for not less than forty minutes. The mixture is agitated thoroughly during this period by means of a mechanical stirrer (1500 revs. per minute). The inside of the flask is then rinsed down with a few c.c. of alcohol, and the heating continued for a very short time at 70° C. The subsequent reduction of the nitrate with Devarda's alloy and the distillation of the resulting ammonia are carried out in the usual way.

E. A. White[60] states that low heat tests of nitroglycerin have been attributed to the presence in the nitrating acids of iodine derived from the sodium nitrate. Examination of a cargo of the latter showed it to consist of three varieties: white, pink, and discoloured. The pink variety showed the highest percentage of iodine, *e.g.*, 0·0168%, some crystals giving as high as 0·044%. The heat test of nitrogen is affected if the iodine content in the nitric acid exceeds 0·005%. Sodium nitrate with less than 0·01% of iodine produces nitric acid that is practically free from iodine. When nitric acid was manufactured from the pink sodium nitrate by the Valentiner process, most of the iodine was driven off from the still charge in the last stages and was found in the weak nitric acid in the back jars.

H. D. Richmond,[61] after giving a *résumé* of various methods which have been proposed for the determination of nitroglycerin and of some experiments of his own on the subject, describes a method in which alcoholic soda is added to a solution of nitroglycerin, and, after standing, the excess alkali is titrated with acid, using phenolphthalein. As accuracy depends partly on the final alcoholic strength, alcoholic acid may be used. The addition of a small quantity of hydrogen peroxide is recommended to prevent discoloration. The method is intended primarily for medical solutions.

Witt[62] states that in the determination by the nitrometer of the nitroglycerin and trinitrotoluene content in powders, severe explosions have taken place. The usual practice was to extract the nitroglycerin and T.N.T. with ether in a Soxhlet apparatus, and evaporate the extract on a water bath, not above 50° C. A nitrogen determination was then carried out on a part of the residue. The nitroglycerin content was calculated from the nitrogen determination, and the T.N.T. obtained by difference. On introducing the reagents into the nitrometer, frequently flashes were observed, and during the subsequent shaking severe explosions occurred. The cause of the accidents was traced to the use of impure ether. Using the purest ether no explosions occurred. Some powders used in the war, both of German and of other origins, contained T.N.T. and nitroglycerin. The evaporation of the ether must be complete before introducing the extract into the nitrometer.

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[59] *Ann. Chim. Analyt.*, 1920, **2**, 271; *J.*, 1920, 705A.

[60] *J. S. Afr. Assoc. Anal. Chem.*, 1919, **2**, 7; *J.*, 1919, 795A.

[61] *Analyst*, 1920, **45**, 260; *J.*, 1920, 640A.

[62] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 145; *J.*, 1920, 641A.

In an article recording experiences with waste waters from factories producing war materials, H. Stooff[63] deals with treatment of acid wash waters. Nitroglycerin, in the manufacture of which only small quantities of acid wash waters result, was retained by settling vessels followed by collodion cotton filters.

A. A. Starring[64] patents an explosive composition consisting of nitroglycerin and a desensitising agent comprising carbon tetrachloride and cottonseed oil or other oil miscible with nitroglycerin.

R. E. Collom[65] states that nitroglycerin is now used for shooting oil wells and that it may explode spontaneously after lying in the bore hole for from 36 to 100 hours. D. F. MacDonald[66] gives some explanation of this. In certain shales, particularly those associated with oil and gas, there are local areas containing finely divided pyrites. In the presence of a warm, moist atmosphere, oxidation of the pyrites to sulphate takes place with evolution of heat, the heat evolved in a drill hole passing through such shale being sometimes sufficient to explode a blasting charge if introduced. To avoid such premature explosions, small iron pipes are inserted in suspected holes, withdrawn after ten minutes, and quickly passed through the hand to locate the heated portion, which is sometimes local, either at or well above the bottom of the hole.

The question of the mechanism of the decomposition of nitrocellulose and nitroglycerin has again arisen in connexion with work done by T. M. Lowry, K. C. Browning, and J. W. Farmery[67] on the products obtained by the decomposition of cordite with lime in presence of pyridine. It is concluded that hydrolysis or saponification of the normal type is not the predominant action when cordite is decomposed with lime in presence of pyridine. The suggestion is made that the main action is a decomposition of the nitric ester into a ketone or aldehyde and a nitrite instead of hydrolysis to an alcohol and nitric acid.

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[63] *Chem.-Zeit.*, 1920, **44**, 601.

[64] U.S.P. 1,336,661; *J.*, 1920, 429A.

[65] *Oil and Gas J.*, 1920, **19**, 74, 76, 86; *Chem. Abs.*, 1920, **13**, 2554.

[66] *Oil Trade J.*, 1920, **11**, 114; *Chem. Abs.*, 1920, **13**, 2713.

[67] *Chem. Soc. Trans.*, 1920, **117**, 552; *J.*, 1920, 558A.

R. C. Farmer[68] claims, however, that the primary reaction in the decomposition of these esters by alkalis is a normal hydrolysis, and that the products actually obtained are secondary products formed by the action of the nitric acid liberated. In the case of nitroglycerin, if the oxidising action of the nitric acid is suppressed either by the presence of reducing agents or by 70% sulphuric acid, or if the alcohol is protected from oxidation by continuous abstraction as glycerophosphoric acid, or by the presence of additional nitro groups such as in the case of the partial hydrolysis of trinitroglycerin to dinitroglycerin, it is really obtained as a product of the decomposition.

Nitroglycol and Ethyl Nitrate.

In a review of Stettbacher's book, "Schiess- und Sprengstoffe," Dr. Naoum[69] criticises Stettbacher's statement that no explosive equals nitroglycerin, and points out that it is merely on account of price that nitroglycol does not hold the first place. The author also points out that, while Stettbacher's views would lead to the conclusion that ethyl nitrate is an explosive of low explosibility, this compound has given a lead block test result of 325 c.c., that of T.N.T. being 285 c.c., and of picric acid 300 c.c.

In a reply to this criticism A. Stettbacher[70] states that nitroglycol is unsuitable for use in manufacture of gelatinised powder on account of its volatility and that its use was a war improvisation.

The preparation of the raw materials for nitroglycerin manufacture gave rise to considerable difficulty in Germany during the war. According to Stettbacher,[71] glycerin was prepared from sugar by a special fermentation process with a 25% yield. This so-called "Fermentol" is a brown liquid containing 98–99% glycerin, and was nitrated like ordinary saponification glycerin. In Germany 2,500,000 kg. of nitroglycerin was produced monthly from "fermentation glycerin."

Nitrocellulose.

For a brief review of the recent developments in connexion with nitrocellulose, especially with relation to the wider cellulose industry, readers are referred to a most interesting series of Cantor lectures delivered by C. F. Cross[72] before the Royal Society of Arts.

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[68] *Ibid.*, 806; *J.*, 1920, 639A.

[69] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 7.

[70] *Ibid.*, 165.

[71] *Schweiz. Chem.-Zeit.*, 1919, **42/3**, 417.

[72] *J. Royal Soc. Arts*, 1920, **68**, 726.

Further work carried out during war exigencies has been published during the past year on the preparation and use of wood pulp for the manufacture of nitrocellulose.

S. D. Wells and V. P. Edwardes[73] nitrated successfully wood pulp made from coniferous wood (Jack pine) by both the soda and sulphite processes. The product possessed a high solubility in ether-alcohol and a high nitrogen content. Nitrocellulose made from sulphate pulp did not possess such a good solubility figure. Under favourable conditions wood pulp gave a yield of 150% of nitrocellulose, while cotton gave 160 to 165%. The wood pulp nitrocellulose was made into pyro powder, and although the usual tests on the powder were not carried out, the United States authorities considered that no difficulty would be encountered in this connexion. This was indicated by the amendment of the specifications of the Ordnance Department to allow "wood pulp prepared by any process from coniferous woods" for the manufacture of nitrocellulose, provided it met the other requirements.

R. G. Woodbridge[74] states that considerable difficulty was experienced in attempts to nitrate wood pulp in spite of modifications in method and the use of wood pulp in different forms. On nitrating mixtures of 50% wood pulp and 50% linters almost all difficulties were eliminated, and smokeless powder manufactured from the resulting nitrocellulose proved as good as that made from nitrocotton. Possibilities of future success in the nitration of wood pulp alone for explosives manufacture are discussed. Preparations had been made for the substitution for cotton of a mixture of 50% linters, 25% hull shavings, and 25% wood pulp (both soda and sulphite) for smokeless powders when the armistice was signed.

C. Claessen[75] also draws attention to the difficulties of nitrating wood in the form of paper or flakes, and states that these may be overcome by mixing it in a finely divided condition with cotton. The mixing may be done in the dry state, but is best done wet, *e.g.*, in a hollander, and the mixture is afterwards given whatever treatment may be necessary, such as bleaching etc.

C. G. Schwalbe and E. Becker[76] point out the advantage of a lime boiling in the preparation of wood cellulose for nitrocellulose and artificial silk manufacture. Sulphite wood celluloses contain cellulose dextrins which can be removed by this treatment. Such celluloses lose up to 50% of their pentosan content, their methyl number is reduced, and the product has practically no reducing properties. By treatment of bleached sulphite cellulose with lime an exceptionally pure cellulose is obtained which in the results of its chemical analysis comes very near to cotton.

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[73] *Paper*, 1919, **25**, 180 ; *J.*, 1919, 603A.

[74] *J. Ind. Eng. Chem.*, 1920, **12**, 380 ; *J.*, 1920, 386A.

[75] G.P. 300,844 ; *J.*, 1920, 315A.

[76] *J. prakt. Chem.*, 1920, **100**, 19 ; *J.*, 1920, 512A.

F. L. Barrett[77] describes an improved dyeing test for the detection of impurities in cotton and cotton waste for nitration purposes. The cotton is treated with a mixture of malachite green and formaldehyde and a little sodium bisulphate, and then bleached by the addition of bleaching powder. The colour is immediately discharged from the cotton and the woody impurities show up as green specks.

A. Dubosc[78] discusses the growth, structure, dimensions, and general physical properties of cotton and the bearing of these factors on the production from it of cellulose and of oxy- and hydro-cellulose, and, later, of the nitro- and acetyl-derivatives. The author concurs with the finding of de Mosenthal, that materials of the same chemical composition, having different physical states, produce esters the properties of which vary to a marked degree.

W. H. Gibson, L. Spencer, and R. McCall[79] show that a relationship exists between the viscosity of the solution of a cellulose in Schweitzer's reagent and the viscosity of solutions of the nitrocellulose prepared from it. The property inherent in cellulose to which viscosity is due is transmitted to the nitrated derivative. A table is given showing that high viscosity in the cellulose is accompanied by high viscosity in its derivatives. In a preliminary paper Gibson and Miss L. M. Jacobs[80] discuss the theory and use of the falling sphere viscometer—the instrument used in subsequent work on the viscosity of solutions of cellulose and nitrocellulose.

Reference should be made at this stage to an important monograph by G. Leysieffer[81] on the relation between the viscosity of solutions of cellulose nitrates and the method of nitration. He shows that the type of cellulose, the method of preparation, and the treatment have a great influence on the viscosity of solutions of the nitrocellulose prepared from it. A high α-cellulose content appears to raise the viscosity. Generally nitrocellulose prepared from cotton has a higher viscosity than that prepared from wood cellulose.

The factors influencing viscosity of a solution of nitrocellulose obtained from a given raw material are:—Composition of the nitrating acid; temperature of the bath; time of nitration; proportion of acid to cellulose. The higher the nitric acid content of the mixed acid up to the point where it becomes equal to or exceeds the sulphuric acid content, the higher is the viscosity. Within these limits increase of the dilution also results in increase of viscosity. Nitration at low temperatures gives high viscosities and an extended time of nitration results in a lower viscosity. There is a close relationship between the nitrogen content of a nitrocellulose and the viscosity of its acetone solution. The higher the nitrogen content the higher is the viscosity. All these results refer to nitrocottons produced by the dipping process.

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[77] *J.*, 1920, 81T.

[78] *Caoutchouc et Gutta-Percha*, 1918, **15**, 9501.

[79] *Chem. Soc. Trans.*, 1920, **117**, 479; *J.*, 1920, 541A.

[80] *Ibid.*, 473; *J.*, 1920, 558A.

[81] *Kolloid-chem. Beihefte*, 1918, **10**, No. 5, 145; *J.*, 1919, 234A

In connexion with the determination of the viscosity of solutions of nitrocellulose, it is essential, in order that results obtained by different workers should be comparable, that the composition of the solvent should be accurately stated. W. H. Gibson and R. McCall[82] show that in the determination of the viscosity of nitrocellulose in ether-alcohol (1) of varying composition, (2) with varying concentration of nitrocellulose with varying nitrogen content, there is an optimum ratio of ether to alcohol on both sides of which the viscosity increases steeply. Within the limits stated this optimum ratio does not depend on the concentration of the nitrocellulose, but on the nitrogen content. Experiments were carried out on the influence of nitroglycerin on these solutions. It was found that the optimum composition of an ether-alcohol solvent was not affected by the use of nitroglycerin. Substitutions by nitroglycerin of a small proportion of the ether-alcohol solvent resulted in a solution, the viscosity of which was approximately equal to that of a similar solution in which the equivalent volume of solvent was absent. Nitroglycerin does not seem to act as a solvent when added to solutions of nitrocellulose in ether-alcohol. The viscosity of the solution tends to be increased rather than decreased by such addition.

I. Masson and R. McCall[83] describe similar experiments on acetone-water solutions of nitrocellulose. Similar results were obtained. Viscosities in anhydrous acetone are relatively very high and traces of water have a most marked effect in lowering the viscosity. An optimum composition is reached also in this case, which is not the same for all kinds of nitrocellulose, nor is it quite independent of the concentration.

J. Duclaux and E. Wollmann[84] fractionally precipitated an acetone solution of nitrocellulose by means of water or a mixture of water and acetone and compared the viscosities of the various fractions in acetone solution. The various fractions contained practically the same percentage of nitrogen, and the viscosity results varied from the first precipitate to the last in the ratio of about 46 to 1. A rough constant, which the author calls the specific viscosity of the nitrocellulose, which is independent of the solvent and concentration, is given by the formula $\eta=\eta_0 10^{kc}$, where η_0 is the viscosity of the solvent, k the specific viscosity, and c the concentration.

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[82] *J.*, 1920, 172T.

[83] *Chem. Soc. Trans.*, 1920, **117**, 819; *J.*, 1920, 641A.

[84] *Bull. Soc. Chim.*, 1920, **27**, 414; *J.*, 1920, 528A.

This fractionation classifies the nitrocellulose according to the size of the micelles, and the author proposes to carry out an analysis of nitrocelluloses of various micellar sizes by means of a series of ultrafilters or dialysers. By this means solutions have already been obtained which are very fluid even at concentrations of 15%. Some experiments have been carried out on the osmotic pressure of solutions of nitrocellulose, and the results hitherto obtained have shown that the measurement of this quantity will form the best means of characterisation of the various nitrocelluloses. The osmotic pressure of acetone solutions is greater the smaller the size of the micelles and the smaller the viscosity. Incidentally the authors point out that de Mosenthal's [85] assertion that nitrocellulose dissolved in acetone does not dialyse and does not exercise any osmotic pressure is not true and that the negative results obtained by him were due to the employment of unsuitable membranes.

From the results of the osmotic pressure determinations it is concluded that the lower limits for the molecular weight of the three fractions experimented with are 70,000, 47,000, and 21,000, corresponding to at least 270, 180, and 80 C_6 groups respectively.

It is evident that it is only by the application of physical measurements similar to those just described that an insight can be obtained into the complex relationship existing between the nitrocelluloses and other cellulose derivatives and the parent substance cellulose. The old ideas of considering the technical nitrocelluloses as consisting of mixtures in various proportions of a small number of nitrocelluloses theoretically derived from a given formula for cellulose have been insufficient to explain the almost infinite range of properties of the nitrocelluloses, and the present tendency is to consider the cellulose esters and ethers as a new class of compounds which have little to do with cellulose itself, but are derived probably from the so-called hydrated celluloses. This is the view adopted by K. Hess [86] in an introductory paper on the constitution of cellulose, and he gives the name 'celluxose' to the parent structure of these cellulose derivatives. The further developments of the views expressed in this paper will be watched with interest.

E. G. Beckett [87] has continued the work of Marqueyrol and Florentin on the determination of nitrogen in nitrocellulose by means of the nitrometer. He shows from accurate determinations of the composition of the gas evolved and the amount of nitrogen remaining in the sulphuric acid, that the nitrometric estimation of nitrogen in nitrocellulose gives results which are too low. He has determined the influence of the quantity and concentration of the sulphuric acid used and the effect of allowing the mixture to stand in the nitrometer before being shaken. The best results are obtained by using 15 c.c. of 92·5–94·0% sulphuric acid and by allowing an interval of between a quarter to half an hour to elapse between the introduction of the nitrocellulose-acid mixture into the nitrometer and the shaking. Under these circumstances the error is about 0·7% of the nitrogen.

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[85] *Chem. Soc. Trans.*, 1911, **99**, 711.

[86] *Z. Elektrochem.*, 1920, **26**, 232; *J.*, 1920, 512A.

[87] *Chem. Soc. Trans.*, 1920, **117**, 220; *J.*, 1920, 386A.

In the continuation of a series of articles on the examination of nitrocellulose, A. Schrimpff[88] deals with the determination of ash, foreign matter, and unnitrated cellulose, solubility in ether-alcohol, nitrogen content, and sulphuric esters. He discusses the various methods for determining stability, and concludes that the best test is the 5 grm. 75° C. closed small vessel test.

The patent literature in connection with the nitrocelluloses has been small during the year. The Société Generale pour la Fabrication des Matières Plastiques[89] patents a mechanical dipping process in which the cellulose is nitrated in a vessel with a conical bottom provided with a helical stirrer, the products of nitration being discharged by means of a cock at the bottom. The stirrer ensures intimate contact of the cellulose with the nitrating liquid as soon as it is introduced into the vessel.

J. M. Voith[90] proposes to pulp nitrated cellulose to half-stuff in a pulper with very sharp knives intended only for cutting purposes, then to pulp in a pulper with blunter knives, and finally to grind to the required fineness in a refining engine. It is claimed that by this means a high output is ensured and dead grinding is avoided.

J. Duclaux[91] purifies nitrocellulose by dissolving it in acetone and precipitating the solution by means of benzine or other agent which has no chemical action on the nitrocellulose, but is a solvent for impurities soluble in water. By using a mixture of benzine and water for the precipitation the impurities soluble in either of these agents are removed.

B. van der Laan[92] suggests that the boiling of the nitrocellulose necessary for its stabilisation be carried out in a rotating boiler of wood or acid-resisting metal such as aluminium, in the interior of which paddles or blades may be arranged to subdivide the nitrocellulose to such a degree that its removal can be effected by means of pumps.

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[88] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 17, 38, 53, 91; *J.*, 1920, 314A, 429A.

[89] F.P. 503,939.

[90] G.P. 292,382.

[91] E.P. 130,619; *J.*, 1920, 469A.

[92] E.P. 147,378; *J.*, 1920, 641A.

Nitro-starch.

B. J. Flürscheim[93] patents a method for the stabilisation of nitro-starch by boiling it with an aqueous solution of cyanamide.

The Harburger Chemische Werke Schön & Co. and W. Daitz[94] have patented a method of preparing explosives from carbohydrates. A carbohydrate such as sugar, starch, or cellulose is dissolved in a solvent which may with advantage contain glycerin, and is then reduced by hydrogen in the presence of a catalyst. After hydrogenation is complete the catalyst is removed and the product nitrated.

Gelatin Explosives.

Very little information has appeared during the year on the subject of gelatin explosives. Stettbacher[95] discussed the competition between nitroglycerin explosives and nitro-aromatic ammonium nitrate explosives for blasting purposes. The nitroglycerin explosives have many advantages, their only weak point being their higher price. The plasticity of nitroglycerin explosives is of great value in the blasting of rocks; the powdery form of the non-gelatinous explosives causes great inconvenience. Other advantages of nitroglycerin explosives are their high density, their explosive energy, and the fact that they are easily detonated. Nitroglycerin explosives are, however, very sensitive and easily frozen, but these disadvantages can be overcome by the addition of a liquid aromatic hydrocarbon, *e.g.*, liquid T.N.T. Gelatin-Telsit is an example of such an explosive. It contains 10–15% of dinitrotoluene or liquid T.N.T. and possesses all the advantages without any of the disadvantages of dynamite.

In a further article[96] details are given of a method for the manufacture of nitrogelatin dynamites, and the following typical composition is given:—Nitroglycerin, 22%; dinitrotoluene, 11%; collodion cotton, 1·2%; sodium nitrate, 30%; ammonium perchlorate, 35%; rye flour or woodmeal, 0·8%.

The preparation of liquid nitro-compound mixtures and their use in explosives has been the subject of a patent by J. Christopher.[97] Liquid dinitrotoluene and liquid T.N.T. obtained as by-products are mixed together or with polynitro compounds of benzene in specified proportions, and the resulting liquid used in gelatinous explosives. In this way an explosive is obtained which remains unfrozen at -10° C.

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[93] U.S.P. 1,343,317; *J.*, 1920, 584A.

[94] G.P. 298,949; *J.*, 1920, 735A.

[95] *Z. ges. Schiess- u. Sprengstoffw.*, 1918, **13**, 405.

[96] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 156; *Schweiz. Chem.-Zeit.* 1919, 441.

[97] F.P. 502,081.

The A.-G. Siegener Dynamit Fabrik[98] has protected a process for gelatinising explosives and other materials. Warm nitroglycerin is forced by compressed air through a jet, and the issuing stream draws in and mixes with air and collodion wool which has been whirled up into dust.

Non-gelatinous Explosives.

W. O. Snelling and W. R. Lams[99] have patented an explosive in which nitro-starch is the characteristic ingredient. The stabilising agent such as diphenylamine is dissolved in a heavy mineral oil to prevent colloiding of the nitro-starch. The explosive also contains ammonium nitrate, sodium nitrate, charcoal, and sodium bicarbonate.

J. R. Mardick[100] protects plastic explosive compositions suitable for blasting explosives. These explosives contain a solid fusible nitro-aromatic compound having at least three nitro groups, an oxidiser, and a substance containing silicon, and are plasticised with a relatively small amount of dinitrotoluene. He also patents[101] similar compositions consisting of an oxidising agent, a metallic reducing agent, and a plasticising agent gelatinised with nitro-cotton, rosin, or nitro-starch. J. R. Mardick and F. M. Becket[102] put forward similar compositions containing magnesium silicide.

An explosive, stated to be particularly useful for coal mining, is suggested by J. B. Bronstein and C. E. Waller[103] consisting of a non-explosive mixture of ammonium nitrate and T.N.T. sensitised with nitro-starch, together with sodium nitrate, zinc oxide, and mineral oil.

K. V. Nielsen and J. P. Larsen[104] patent an explosive prepared as follows:—Sulphur, glycerin, pyrolusite, and resin are first melted together. Potassium nitrate and sago flour are then incorporated and finally ammonium nitrate is added. The composition is melted in a closed vessel to a thin liquid, cooled, and ground.

One of the chief difficulties encountered in the manufacture of ammonium nitrate explosives is the caking or setting of the ammonium nitrate. W. O. Snelling[105] proposes to prevent this in an explosive containing 40–90% of ammonium nitrate and 5–20% of nitro-starch by the addition of a pulverulent material of high covering power such as rouge or ochre. The problem is

[98] G.P. 298,420; *J.*, 1920, 676A.

[99] U.S.P. 1,329,211-2; *J.*, 1920, 249A

[100] U.S.P. 1,335,788; *J.*, 1920, 429A.

[101] U.S.P. 1,335,790; *J.*, 1920, 429A.

[102] U.S.P. 1,335,789; *J.*, 1920, 429A.

[103] U.S.P. 1,343,077; *J.*, 1920, 584A.

[104] U.S.P. 1,293,882; *J.*, 1919, 240A.

[105] U.S.P. 1,343,063; *J.*, 1920, 583A.

attacked from another standpoint by the Atlas Powder Co.,[106] who have patented the use of anhydrous copper sulphate in ammonium nitrate explosives to prevent them from becoming moist during manufacture and setting.

A number of ammonium nitrate explosives have been patented which have perhaps a better application as military explosives than as blasting explosives. The Oberhessische Kalk und Stein Industrie G.m.b.H.[107] have patented a process for producing an ammonium nitrate powder in which the time of grinding is reduced by previous steaming of the charcoal ingredient at 110°–120° C.

D. de Vulitch[108] has protected numerous mixtures containing ammonium nitrate and one or more of the following:—Silicon, ferro-aluminium, ferro-silicon, magnesium silicide, sulphur, and aluminium.

C. Manuelli and L. Bernardini[109] protect explosive products obtained by melting together ammonium nitrate, guanidine, or biguanide nitrate; or ammonium nitrate, dicyanodiamide, with or without nitroguanidine, in such proportions that the product melts below 130° C. It is claimed that the mixtures have high explosive power and great stability.

The use of dicyanodiamide in explosives has also been investigated by J. Baumann.[110] Mixtures of dicyanodiamide with ammonium nitrate and with potassium chlorate were made up and lead block tests were carried out on these mixtures. The explosive action with dicyanodiamide in the ammonium nitrate mixture was 17% higher, and that in the potassium chlorate mixture 72% higher than the explosive action of T.N.T. Dicyanodiamide is in itself not explosive; its heat of formation has not yet been determined. The mixing of dicyanodiamide with ammonium nitrate and the transport and manipulation of the mixture are free from danger. G. Gin[111] has taken out a patent on these lines. E. Müller[112] patents a process for producing an explosive by mixing ammonium nitrate with petroleum or other hydrocarbons or hydrocarbon derivatives, while in a molten state, under slight pressure, with or without other ingredients.

Badische Anilin u. Soda-Fabrik[113] protect the use of nitro-urea or its compounds in explosives. Mixtures of nitro-urea with potassium and ammonium nitrates are given. As nitro-urea is not very sensitive, a strong detonator is required.

[106] E.P. 134,523-4; *cf.* U.S.P. 1,340,975; *J.*, 1919, 604A.

[107] G.P. 303,370; *J.*, 1919, 879A.

[108] F.P. 502,277, 502,400, 502,401.

[109] E.P. 138,371; J., 1920, 281A.

[110] *Chem.-Zeit.*, 1920, **44**, 474; *J.*, 1920, 583A.

[111] F.P. 502,121.

[112] E.P. 152,199; *J.*, 1920, 803A.

[113] G.P 303,929; *J.*, 1920, 208A.

The Oberschlesische Sprengstoff A.-G.[114] has patented a method by which explosives of a dusty nature, and which can be detonated only with difficulty, may be converted into granular safety explosives which can be readily detonated, by mixing them with finely-divided fusible carbonaceous substances such as naphthalene, resin, or dextrin, and agitating the mixture with steam.

G. A. Krause u. Co. A.-G.[115] protect a new method for the preparation of chlorate explosives, which consists in the rapid evaporation, by a gaseous drying agent, of a spray of chlorate solution containing charcoal or other material in suspension.

F. Müller[116] proposes the use of alkali benzoates as ingredients of chlorate explosives. A suitable composition consists of three parts potassium chlorate, 1 part charcoal, and 1½ parts sodium benzoate. A plastic chlorate explosive has been patented by J. M. Brown[117] consisting of 60 parts of alkali chlorate, 8 of drying oil, 22 of vegetable flour with small proportions of nitroglycerin, vaseline, and magnesium carbonate, while R. L. Hill[118] protects a composition consisting of ammonium perchlorate, nitro-starch, and a compound of a metal which will combine with chlorine, and an oil to prevent dustiness. C. Bunge[119] proposes to increase the sensitiveness of perchlorate explosives by introduction of potassium permanganate as a catalyst. The Fürstlich Plessische Miedziankit Fabrik[120] propose to improve the keeping properties of chlorate explosives which contain a liquid volatile ingredient by addition of kieselguhr, and have patented[121] a process for granulating and compressing explosives by addition of a mixture of formaldehyde and albumin.

Owing to the shortage of nitrates in Germany during the war, proposals were put forward to replace ammonium nitrate explosives by chlorate explosives. A. Spielmann,[122] in this connexion, states that chlorate explosives are very brisant, and before they can be used in work where shattering effect must be avoided (*e.g.*, in coal mining), they must be made much milder in character. Some regulation is effected by selection of detonator. Tables are given of results of experiments with various chlorate explosives made by different firms.

E. Kohl[123] describes an explosion of cheddite at the potash

[114] G.P. 298,448; *J.*, 1920, 803A.

[115] G.P. 299,630; *J.*, 1920, 803A.

[116] G.P. 307,039; *J.*, 1920, 136A.

[117] U.S.P. 1,309,014; *J.*, 1919, 659A.

[118] U.S.P. 1,334,303; *J.*, 1920, 386A.

[119] G.P. 303,289; *J.*, 1920, 208A.

[120] G.P. 313,016; *J.*, 1919, 879A.

[121] G.P. 304,000; *J.*, 1920, 430A.

[122] *Z. ges. Schiess- u. Sprengstoffw.*, 1916, **11**, 131.

[123] *Ibid.*, 1920, **15**, 148.

mines at Wittenheim. The explosive in question was cheddite, composed of sodium chlorate 90%, paraffin 7%, and vaseline 3%. The individual cartridges were wrapped in paraffined paper and packed in boxes. On exposure to moist atmospheric conditions, the sodium chlorate dissolved and the solution came through the wrappers. During warm storage, the salt crystallised out again on the cartridge wrapper and the inside of the packing case. The friction produced on opening the case was sufficient to ignite the combustible packing material. In the same store, there were a great amount of explosive and over 10,000 detonators charged with about 20 kg. of mercury fulminate. When these ignited the whole store exploded.

In the amended German railway regulations[124] details are given of a large number of explosive compositions.

F. Torelli[125] claims the use of dicyanodiamidine chlorate or perchlorate, guanidine chlorate or perchlorate as substitutes for alkali chlorates or perchlorates in explosive mixtures.

The use of coumarone resin is protected by A. Wilhelmi,[126] who advocates mixtures of it with nitrates, chlorates, or even liquid air or oxygen. L. O. Bryan and W. R. Swint[127] put forward a blasting explosive containing a low proportion of nitroglycerin, T.N.T., and sodium nitrate, together with wood pulp, corn flour, and sulphur, while W. R. Swint[128] patents two low-freezing plastic guncotton blasting explosives, one, a dynamite consisting of guncotton of high nitration 40 pts., liquid nitroxylenes 25 pts., and sodium nitrate 35 pts., the other a gelatin-dynamite containing guncotton of high nitration 35 pts., guncotton of low nitration 1 pt., liquid nitroxylenes 40 pts., and sodium nitrate 24 pts.

A rather unusual type of explosive has been patented by the J. D. Riedel A.-G.,[129] who state that an alkyldichloroamine such as methyldichloroamine, absorbed in kieselguhr, can be detonated by mercury fulminate.

Pine bark meal and similar materials under various names have lately come into prominence, more especially in Scandinavia. G. A. Hedburg[130] claims the use of pine bark meal and pine cone meal in granular explosives, of which ammonium nitrate or perchlorate is the chief constituent. It is held that they increase the detonating effect and prevent absorption of moisture.

The patents taken out during the war by Germany and other countries in connexion with nitroglycerin, dynamite, ammonium nitrate blasting and chlorate blasting explosives, and also liquid air explosives have been summarised.[131]

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[124] *Ibid.*, 1919, **14**, 46, 404; 1920, **15**, 94. *Sprengstoffe, Waffen, und Munit.*, 1916, **11**, 76, 151, 190; 1917, **12**, 5; 1919, **14**, 144; 1920, **15**, 12.

[125] F.P. 502,522.

[126] G.P. 300,040; *J.*, 1920, 677A.

[127] U.S.P. 1,327,859; *J.*, 1920, 249A.

[128] U.S.P. 1,309,553; *J.*, 1919, 659A.

[129] G.P. 301,799; *J.*, 1920, 735A.

[130] E.P. 140,967, 142,763; U.S.P. 1,335,785; *J.*, 1920, 429A.

R. S. Lewis,[132] in giving a description of the compositions and characteristics of explosives in common use, reproduces a table given by the du Pont Company showing the quantity relation between equivalent charges of dynamites of different strengths.

In the course of an article summarising the various uses to which explosives may be put in agriculture, A. Stettbacher[133] states that a beginning is now being made in the development of agricultural blasting on scientific lines. E. Fels[134] discusses the use of non-nitroglycerin ammonium nitrate explosives for tree stumping and felling.

An ingenious invention has been patented by W. O. Snelling.[135] He claims a process in which a fertiliser such as phosphatic rock, ground to a fine powder, is granulated and mixed into an explosive. Owing to their form the granules do not interfere with the explosive, but break up into powder at the moment of detonation.

C. E. Munroe and S. P. Howell have reported investigations on the use of T.N.T. as a blasting explosive,[136] and also of Modified T.N.T., a mixture of Trojan grenade powder (of which large surplus stocks were available) and T.N.T.[137] The mixture was found on explosion to give larger craters than T.N.T. alone.

Liquid Air or Oxygen Explosives.

The release from control of the raw materials used in blasting explosives has proved unfavourable to the competition of liquid air explosives.

J. Thorburn,[138] in a review of the history, practice, and prospect of liquid oxygen explosives, states that it is perhaps too early to forecast the future of these explosives, but it is unlikely that, under normal conditions, they will replace ordinary explosives to any appreciable extent. Since the war, their importance has diminished, owing to the renewed possibility of obtaining ordinary explosives. The existence of the necessary plant in Germany might be expected to favour the preference of liquid oxygen explosives there, but ordinary explosives have already displaced them in some districts. In

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[131] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 36, 51, 76.

[132] *Min. and Sci. Press*, 1919, 245.

[133] *Z. angew. Chem.*, 1920, **55**, 203.

[134] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 113.

[135] U.S.P. 1,316,396 ; *J.*, 1919, 838A.

[136] *U.S. Dept. Agric., Circ.* 94, 1920.

[137] *U.S. Bureau of Mines, Reports of Investigations*, June, 1920 ; *J.*, 1920, 647A.

[138] *J.*, 1920, 317R.

Alsace-Lorraine, on the other hand, the situation is still obscure owing to the influence of the French Government tax on explosives.

Numerous articles[139] have appeared during the year on the subject of liquid oxygen explosives, but there have been very few advances.

Numerous patents covering the design of cartridge, the explosive mixture, the absorbent, and the addition of metallic powders, have been taken out by Les Petits Fils de Francois de Wendel et Cie.[140]

UTILISATION OF WASTE EXPLOSIVES.

At the termination of the war enormous stocks of propulsive and high explosives remained for disposal. As most of these would deteriorate on storage, and some of them very rapidly, numerous attempts were made to use up the surplus as or in blasting explosives. Reference has already been made to C. E. Munroe and S. P. Howell's investigations of T.N.T. and of the mixture of Trojan Grenade Powder with T.N.T.

G. Gariboldi[141] gives an account of experiments carried out with ballistite, solenite, T.N.T., and picric acid, made at Cengio Factory, to determine their values for industrial work or as agricultural explosives. Powdered ballistite, especially if initiated by a mercury fulminate detonator, is well adapted for work in mines, as also are T.N.T. and picric acid in crystalline or pulverulent form. Solenite and similar powders behave like ballistite, and must be finely powdered and strongly tamped, but all these powders are less well adapted for blasting in hard rock than T.N.T. or picric acid. The explosion gases from ballistite are not injurious. An illustrated description is given of results obtained in the loosening of soil of various types under different conditions with ballistite, T.N.T. and picric acid, and the specific advantages of each are discussed for given types of work.

An alternative method[142] of utilising ammonium nitrate high explosives is to extract the ammonium nitrate with water, add the solution to peat and dry the mixture. This "nitric peat" has about the same value as sodium nitrate as a fertiliser.

PERMITTED EXPLOSIVES.

Very little work has been done on permitted explosives during the past year. The reduction of the number of different compositions of similar character which took place in 1919 has been carried further during 1920. The high price of perchlorates and ammonium oxalate has rendered the manufacture of many compositions prohibitive, so that the main constituents of permitted explosives are limited to a few materials such as ammonium nitrate, sodium chloride, nitroglycerin, T.N.T., woodmeal, etc.

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[139] A. Pol, *Bull. Soc. Ind. Min.*, 1919, 237. C. Forch, *Prometheus*, 1919, 91. H. Diederichs, *Stahl und Eisen*, 1920, 52; *J.*, 1920, 315A. *Iron and Coal Trade Rev.*, 1920, 318. *Colliery Guardian*, 1920, 655. E. Neumann, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 45.

[140] F.P. 498,105-9, 499,434-7, 499,439, 499,462-4, 500,343.

[141] *Giorn. Chim. Ind. Appl.*, 1920, **2**, 10.

[142] *J. Ind. Eng. Chem.*, 1920, **12**, 390.

Numerous re-tests of existing permitted explosives have taken place, to allow of the transfer of the manufacture from one factory to another. Two new compositions[143] have passed the test—Monarkite No. 2 with a pendulum swing of 2·46 in., at a charge limit of 32 oz., and Super Excellite No. 4 with pendulum swing of 2·77 in. and charge limit 22 oz.

The Belgian Government[144] give the compositions of the following five ammonium nitrate explosives which have been placed on their permitted list (S.P.G.). These are "Flammivore III. bis" made by Société d'Arendonck, "Viking Powder No. 1" and "Viking Powder No. 2" made by Nobel's Explosives Co., Ltd., "Matagnite" made by the Société Anonyme de Dynamite de Matagne, and "Explosif de Baelen No. 1" made by Compagnie La Forcite.

Testing of Blasting Explosives.

L. Crussard[145] contributes a theoretical paper on the propagation of combustion, distinguishing between deflagration and detonation, and discussing the effect of various factors on the stability of the propagation. The explosion wave is also discussed, and the manner in which its velocity of propagation depends on the density of the charge.

E. A. Mann[146] describes a standard method of carrying out the D'Autriche test used in the laboratory of the Government Analyst, Western Australia. Fixed distances are observed between the firing detonator and the first velocity detonator as well as between the two velocity detonators. The uniformity of these distances is insured by the use of a metal gauge which forms punctures in the cartridges before inserting the velocity detonators. The two latter should always be placed 200 mm. apart, and the first velocity detonator is inserted at 90 mm. from the end of the cartridge in which the firing detonator is inserted.

A report[147] is given of the work carried out during 1914 in the testing gallery of the Knappschafts Berufsgenossenschaft in Derne; 100 m. were added to the testing gallery at the end of 1913, making the total length 200 m. The height appears to be 1·70 m. and the breadth 1·55 m. It was found that the explosions were much more violent as a result of the increased length.

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[143] *Explosives in Coal Mines Orders*, 1920, Aug. 25.

[144] *Ann. Mines de Belgique*, 1920, **21**, 1259.

[145] *Technique Moderne*, 1920, **14**, 243, 295.

[146] *Ann. Rep. of the Government Analyst, Western Australia*, 1919, 1920.

[147] *Glückauf*, 1915, 921.

E. H. Schulz[148] describes a blast meter consisting of a graduated series of cups, each having a depth equal to its diameter. A sheet of a standard strength of paper is laid over the cups and clamped by a cover. When a test is made, the smallest opening ruptured measures the force of blast at that point, and also the strength of the explosive for shattering effect. The paper is standardised by the Mullen test machine, which gives practically the rupturing pressure in pounds per square inch for the area of the paper tested. Recommendations are made as to the grading of the sizes of the openings, and as to further investigations which are necessary. Samples of various grades of paper are given.

S. P. Howell[149] describes a new pendulum device for measuring the sensitiveness of explosives to frictional impact. The Bureau of Mines has adopted this method as it gives more uniform results than is possible with the ordinary broomstick and raw hide mallet tests. The explosive is placed in grooves in a steel anvil which is struck a glancing blow by a swinging steel shoe faced with hardwood fibre, or for the more severe tests, unfaced. The relative sensitiveness of explosives by this apparatus agrees with that by the older methods. Results are given of explosives of various types.

In an article[150] discussing the effect of the detonation of hollowed charges of explosive, A. Marshall states that the discovery of this effect ascribed to E. Neumann was originally made much earlier by C. E. Munroe of Washington. Munroe found that the more he hollowed out the face of an unconfined cylinder of a high explosive resting on an iron plate, the greater was the depth of the depression formed. A cylindrical hollow was as effective as, if not more so than, a conical hollow. No practical use has been made of this effect, but it is of interest as throwing light on the nature of the detonation wave.

PROPULSIVE EXPLOSIVES.

The amount of information that has come to light regarding the developments in propellant powders is disappointingly small, and beyond an article in the *Giornale di Chimica Industriale ed Applicata* already referred to, no full account has appeared of the war activities of the late belligerents in the development of propellant powders. The comparative immunity of the allied Powers from any form of blockade is reflected in their freedom to make use of the usual raw materials for the production of propellants, and forms a marked contrast to the alterations and subterfuges forced by sheer necessity upon the Central Powers.

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[148] "*Professional Memoirs*," 1919, 325.

[149] *U.S. Bureau of Mines, Tech. Paper* 234; *J.*, 1920, 314A.

[150] *J.*, 1920, 35T.

Nitrocellulose Powders.

This type of powder, while of comparatively recent introduction into the British Service, has for a long time been the principal propellant in France, Germany and America. Its many points of superiority over cordite, particularly with reference to erosion, and its constant ballistics over a range of temperatures,[151] have made it a favourite, particularly for land service work, but the influence of its hygroscopicity on ballistics, to guard against which expensive containers are necessary, has been a recognised drawback.[152] A very full account of the American method of manufacture has appeared in *Arms and the Man*[153]; this account deals with the dehydration, incorporation, pressing, drying, and water soaking of the grains and subsequent glazing of the powders. Details of ballistic testing are also given. In America, notwithstanding its favourable position with regard to cotton supplies, the problem of the substitution of wood pulp for cotton in the manufacture of nitrocellulose powders was kept in view. The du Pont Co. worked out a powder for the 3-in. field gun with a product made from 50% linters and 50% sulphite pulp. It was satisfactory in ballistics and stability, requiring 8% less solvent for gelatinisation, but 10% longer time for dehydration. In August, 1918, owing to the drought, there was an anticipated cotton shortage, and steps were taken for the adoption of a mixture of 63% linters, 23·5% hull shavings, and 13·5% wood pulp; however, owing to the armistice the product was never actually made.[154]

In Germany, on the other hand, the restriction of cotton supplies soon forced the nation into the adoption of wood cellulose. Apparently the difficulties experienced in America with the shortness of the colloid produced from nitrated wood cellulose had been overcome by the Germans, for their nitrocellulose powders were made eventually wholly from this material as basis, and it is their intention to employ this type of nitrocellulose solely in future.[155] Furthermore, it was found possible to nitrate the treated wood directly without converting it previously into crêpe form.

In Germany[156] pure nitrocellulose powders are employed for rifles, machine guns, and light artillery. The nitrocellulose powders consist of a mixture of nitrocottons of 13·2% nitrogen and 12·4% nitrogen respectively, the ratio being two parts of

[151] *Field*, April 16, 1920, 542.

[152] *National Service*, Nov., 1919, 300.

[153] C. S. Landis, *Arms and the Man*, Oct. and March, 1920, 3 and 5.

[154] R. G. Woodbridge, *J. Ind. Eng. Chem.*, 1920, **12**, 380; *J.*, 1920, **386A**.

[155] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 148.

[156] Gallo, *Giorn. Chim. Ind. Appl.*, 1920, **2**, 628.

the former to one part of the latter. The mixed nitrocottons, after elimination of water, are gelatinised with ether and alcohol (2 parts of ether to 1 part of alcohol) in the presence of 2% of camphor, which regulates the velocity of combustion, and 1% of diphenylamine, "centralite," or sodium oxalate, to effect stability. The dough is pressed and dried in the usual way, the resulting grains, after drying, being moistened with a solution of camphor or "centralite" in alcohol, re-dried, and then lightly graphited. During the war a certain amount of difficulty was experienced in obtaining the moderating and stabilising materials. Camphor, which had been supplied previous to the war exclusively from Japan, was prepared synthetically by the oxidation of isoborneol with potassium permanganate. In many cases camphor was replaced by "centralite," while, owing to the shortage of methyl alcohol employed in the manufacture of the latter, the diethyl equivalent, diethyldiphenylurea, was often substituted for "centralite." The substituted urea, Akardit, was also employed. In Germany the recovery of the ether and alcohol in the manufacture of nitrocellulose powders was effected by scrubbing the vapours coming from the drying chambers by means of a stream of sulphuric acid flowing down towers in the usual manner. Large installations were erected for the recovery of these solvents from this solution.

On the question of drying of powders and solvent recovery several methods have come to notice.

I. M. Voith[157] proposes to use water or aqueous solutions of alcohol, acetone, salts, etc., for the removal of solvent. The process is said to be free from danger and the eventual drying to be more rapid.

L. Gathmann[158] proposes a method of drying powders which consists in gradually raising the temperature of the condenser so as to prevent the condensing of all the solvents or vapours, with the object of keeping the surface of the powder in the drying chamber moist and thus prevent bottling up of the solvent in the interior of the powder. By this means the powder is said to be dried in a much shorter period, a larger percentage of solvent is recovered, and a more reliable and stable powder produced.

G. Weissenberger[159] outlines a drying plant which consists of a tunnel having a separate compartment at each end, with inner and outer doors, and serving as intermediate chambers for admitting or discharging bogeys containing the explosive without loss of vapour or heat from the main tunnel. By means of a fan air is circulated through the tunnel in an opposite direction to the passage of the explosive, and after leaving the tunnel passes

[157] G.P. 302,560; *J.*, 1920, 208A.

[158] U.S.P. 1,289,150; *J.*, 1919, 200A.

[159] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, 15, 33; *J.*, 1920, 314A.

successively through a precooler and into final coolers. The cooled air from the latter is utilised as a cooling agent for the precooler, and at the same time undergoes a preliminary heating before returning to the heater and tunnel. In the final coolers the temperature is lowered to -50° C., and by this means the air is completely freed from moisture and volatile solvent and acquires a high drying capacity. In comparison with ordinary air or vacuum dryers, the apparatus requires only half the fuel consumption, provides continuous and more complete drying and recovery, and demands little supervision.

Attention is directed to an article which has appeared describing various processes for the recovery of volatile solvents, including the Bregeat, Crepelle Fontaine, Collard and Société de l'Air Liquide, and that employed at Tubize.[160] These methods have as a basis scrubbing the vapours with cresol, sulphuric acid of various strengths, and direct condensation by refrigeration, in the former cases various types of scrubber being introduced to effect sufficiently intimate contact between the vapours and the absorbing medium.

It has been suggested[161] to increase the density or diminish the porosity of nitrocellulose grains by raising the amount of collodion cotton added to the explosive for gelatinising purposes from 20–25% to 27–30%. To prevent the newly pressed powder from becoming porous when treated with water, the collodion cotton may be raised to 45%.

In connexion with the general ballistic efficiency of nitrocellulose powders on storage, it is of interest to point out that after the battle of the Marne French stocks were near exhaustion, and powder which had been sunk in the harbour of Toulon after the Jena disaster was taken up again, and when dried gave unimpaired ballistics. For this reason it was decided to sink the excess material from the war in the lakes of the Pyrenees, the water of which at certain depths maintains a fairly uniform temperature of 5°–6° C. In these favourable conditions it is estimated that the powder can be maintained in a usable condition for 24 years, as against the normal 5–6 years.[162]

An interesting development in the case of nitrocellulose powders is the introduction of powders containing zinc, tin, and various alloys, for the purpose of diminishing the metallic fouling[163] and hence making for increased accuracy. During the war the French discovered[164] that by including some tin foil with the charge or by plating the base of the shell with tin or lead, the copper fouling in guns like the 4·7 British howitzer was greatly diminished. It is considered that the metal forms a brittle alloy with the copper in the bore, and this alloy is easily swept out. The method of incorporating the decoppering metal with the powder in the normal course of manufacture has certain obvious advantages, particularly in the case of rifles or machine guns. Powders of this nature known as du Pont 15½ and du Pont 17½ have been tested in trials for the development of an ammunition for the American Olympic match rifle team, and have been found very satisfactory in reducing metal fouling, and the firing of a couple of sighting rounds with this powder clears the barrel effectively after using ammunition loaded with ordinary nitrocellulose powder.

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[160] *Caoutchouc et Gutta-Percha*, 1919, 9980.

[161] I. M. Voith, G.P. 300,737; *J.*, 1920, 207A.

[162] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 29.

[163] C. LeB. Henning, U.S.P. 1,336,463; *J.*, 1920, 803A.

[164] Crossman, *Arms and the Man*, June 15, 1920, 5.

Powders with a Nitroglycerin Basis.

An interesting account of the development of progressivity in powders of this type has appeared.[165] The account starts with the tubular form as in Cordite M.D. size 5.2 and passing on to multi-tubular M.D., which burned too progressively and became dangerous except in reduced loads, leads up to the coating of the grain with inert material to delay ignition, as patented by F. W. Jones in 1898; the latter method may be regarded as the precursor of the modern progressive nitrocellulose powder.

The production of a progressive nitroglycerin powder in which the effect is produced by disposing an interior sheet of brisant colloidal powder containing nitroglycerin between exterior sheets of less brisant colloidal powder also containing nitroglycerin, the sheets being caused to adhere by mechanical pressure with or without the aid of a solvent, has been patented.[166] It would appear to be a powder as described in this patent that was employed by one of the Allies for their long range guns. The powder used by another of the Allies was about 2½ feet long, roughly elliptical in cross-section, the axes being about 1 in. and 1½ in. respectively.[167]

An account to hand[168] of the German method of manufacturing powders throws some light on the position during the war. In Germany nitroglycerin powders were used for naval purposes and for heavy artillery; incorporation was effected by wet mixing the nitroglycerin and nitrocellulose in accordance with the ballistite process, drying the mixture to a cake on hot rolls, and then gelatinising in a mixer of the Werner and Pfleiderer type with acetone, stabilisers like diphenylamine, "centralite," or sodium oxalate being added at this stage. The gelatinised material was then worked up into grains in the usual manner.

[165] *Field*, July, 1920, 2.

[166] J. Delpech, U.S.P. 1,316,360.

[167] *J.U.S. Artillery*, May, 1920, 469.

[168] G. Gallo, *Giorn. Chim. Ind. Appl.*, 1920, 2, 629.

Of particular interest is the non-solvent powder produced at Düneberg in the Rottweil Factory. This powder, which is made according to the ballistite process, consists of a mixture of 73% collodion-cotton of 11% nitrogen, 25% nitroglycerin, and 2% "centralite." The ingredients, after mixing, are gelatinised into a homogeneous mass on warm rolls at a temperature of 80° C. The gelatinised material is then transferred to a double-walled cylinder which is heated at a temperature of 80° C., and is there expressed, under a pressure of about 12,000 atm., in the form of ribbon or tubes, and is then cut and graphited in the usual manner. Powders prepared in this fashion can be used directly after making, and have not to be submitted to any drying operation. This has a special advantage in the case of bigger sizes. The composition is more uniform than in those made with acetone, and is superior in ballistics owing to the fact that there is no residual solvent. The powder appears to have given some trouble in rolling, for at Düneberg during the war there were 50,000 ignitions without, however, any definite explosion being observed.

In connexion with non-solvent powders, the use of urethanes, which contain two groups attached to the nitrogen atom, one group being a benzyl group, has been patented.[169]

With reference to the phenomenon of muzzle flash, it has been proposed[170] to reduce this by treating a stabilised nitroglycerin-nitrocellulose powder with a solution of camphor, and after drying with a 20% solution ot potassium tartrate or potassium oxalate; it has also been proposed[171] to add to a nitroglycerin-nitrocellulose powder at the incorporating stage a percentage of carbohydrate-like substances, preferably starch. On the other hand, it has been stated[172] that nitronaphthalene used as moderant in ballistite is the chief cause of muzzle flame with this powder.

It has been proposed to stabilise powders by the addition of betaine[173] or compounds of betaine, and to improve the stability and plasticity[174] of powders by the addition of such anilides of organic acids as have the imide hydrogen atom replaced by a radicle, methyl- or ethyl-acetanilide being excepted.

Miscellaneous Propellant Powders.

Owing to the glycerin shortage in Germany the necessity for a substitute for nitroglycerin for powders became very urgent. It was found that dinitroglycol was not a suitable substitute on account of its high volatility, and its use was restricted to explosives for mining purposes. On the other hand, it was found possible to employ in part, or even wholly, trinitrotoluene as a substitute for nitroglycerin in propellants, but naturally, in order to obtain a ballistically efficient powder, it was necessary to employ a nitrocotton of a rather higher nitrogen content than had been used for nitroglycerin powders. At Düneberg a powder was made as follows :—The mixing was carried out in a large cylindrical vessel fitted with compressed air and steam. Into the cylinder was first introduced water, then nitrocellulose and "centralite." The whole was heated to 85° C. and the trinitrotoluene then added, agitation with air being maintained until the trinitrotoluene filled the capillaries of the nitrocellulose. The whole was then centrifuged to eliminate water and then rolled on hot rolls and pressed in a jacketed cylinder as in the case of the non-solvent nitroglycerin powders. Total substitution by trinitrotoluene could not be employed in the case of the smaller sizes of pressed powder.

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[169] W. Rintoul, U.S.P. 1,348,741; *J.*, 1920, 641A.

[170] C. J. Weld Blundell, F.P. 458,372.

[171] O. Silberrad, U.S.P. 1,349,983; *J.*, 1920, 676A.

[172] Hausen, *Mitt. Artillerie und Geniewesens*, 1916, 177.

[173] F.P. 476,931.

[174] G.P. 296,591.

It is reported that a peculiar ballistic effect was found to be associated with hexanitroethane ; this material when mixed in nitroglycerin or nitrocellulose powders has a marked controlling effect on the rate of burning of the colloid, and by regulating suitably the composition of the mixture, excellent effects could be obtained. It is surmised that this material may have been used in the long-range guns that shelled Paris.

It has been suggested[175] to make a smokeless powder by employing instead of nitrocellulose, nitro-starch, and mixing this with an agent, *e.g.*, liquid T.N.T., which does not gelatinise the nitro-starch during the mixing process, and subsequently heating the mixture to 60°–90° C. to effect gelatinisation. It has also been proposed[176] to make propellants relatively insensitive to shock by employing, in conjunction with nitrocellulose, the compound ($C_3H_6N_6O_6$) obtained on the nitration of hexamethylenetetramine, gelatinisation being effected by volatile solvents like ether-alcohol or acetone, or non-volatile solvents like di- or tri-nitrobenzene, toluene, anisole, or similar substances.

As a substitute for propellants made from the ordinary raw materials, the Central Powers employed to a large extent a species of black powder.[177] This powder, which had been employed to a certain degree in Austria prior to the war, consisted of a mixture of 85 parts of ammonium nitrate and 15 parts of charcoal. The ammonium nitrate and charcoal, to which were added 25 parts of water, were mixed in a Werner and Pfleiderer machine. The thick solution was passed on to rollers heated at 130° C. and the cake then pressed at 1500 atm. pressure into the desired form. The Krause A.-G. developed a rather neat method in which the concentrated solution of ammonium nitrate carrying in suspension the finely-divided charcoal was centrifuged at a high velocity and thus resolved into a dense mist which was met by a counter-blast of hot air and dried. The material was collected, pressed, and formed into rings. An output of about 3000 tons per month was maintained. The material was used in the form of rings weighing 170–200 g. or small cylinders weighing 50 g. The best ballistic effects were obtained by making half the propellant charge in the form of short tubes. In filling up the upper half of the cartridge with two rings of the nitrate or a corresponding weight of small cylinders, ballistics equal to nitrocellulose powders were obtained. A certain amount of difficulty was experienced owing to the hygroscopicity of the ammonium nitrate, but this was overcome by packing the powder in suitable receptacles. A powder rather similar to this German product has been devised by F. I. du Pont[178]; it consists of a mixture of 92½ parts of ammonium nitrate with 7½ parts of a binding material, preferably nitrocellulose, which is colloided with amyl acetate; this powder, while eliminating muzzle flash, is also less erosive than the usual types of propellant.

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[175] W. O. Snelling, U.S.P. 1,305,946 ; *J.*, 1920, 283A.

[176] G.P. 298,539.

[177] Gallo, *loc. cit.*

EROSION AND CORROSION.

The phenomenon of gun erosion is as much a matter of the gun lining as of the nature of the propellant, so that it seems scarcely to fall within the ambit of the present review; however, it is of interest to draw attention to some records that have come to notice since the last report. It is pointed out[179] that a case-hardening effect is a preliminary to the development of gun cracks and corrosion, this case-hardening being produced probably by the action of temperature and the gases of combustion of the powder, as the phenomenon is found to occur in the gun chamber as well as along the barrel. The use of manganese, tungsten, or molybdenum steels is advocated as being the most effective in withstanding erosion. In practice it would be sufficient to limit the lining of the rear portion of the gun barrel where erosion is most rapidly produced and a fine finish is not necessary, as the rear part of the barrel is eroded long before the gun ceases to give effective service.

The dynamic action of the explosion, which has received little attention hitherto, is now being studied, and there are also indications of nitration of the steel.[180]

It has been stated[181] that the mantle tube guns of the Bethlehem Steel Co. have shown better durability than British wire-wound guns. This is attributed to the employment of a pure nitrocellulose powder by the Americans rather than to any particular merit in the construction of the guns.

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[178] U.S.P. 1,341,207; *J.*, 1920, 529A.

[179] Bennington, *Sci. Amer.*, 1920, 44. Demenge, *Rev. Gén. Sci.*, 1918, 579.

[180] *Mitt. Artillerie und Geniewesens*, 1916, 177.

[181] *Ibid.*, 1914, 1281.

With regard to the phenomenon of corrosion, confirmatory evidence[182] has come to light of the corrosive influence of the residue from perchlorates containing initiating charges in the gun barrel. The futility of certain so-called cleaning mixtures is well brought out in the article in question.

BALLISTICS.

An interesting series of articles[183] has appeared on the combustion velocities of colloidal propulsive powders; it is stated that experiments carried out on cylinders of nitroglycerin powders, placed vertically and ignited either at the top or in a defined current of air at the bottom, indicated from measurements of the conical burning surface, constancy of combustion velocity normal to the surface and variation of combustion velocity along the surface with surface conditions and air currents. The discrepancy between the normal combustion velocity as measured from the cone angles and those deduced from Petavel's results is found to be due to loss of solid particles from the rods during combustion. The combustion velocity determined in free air cannot be used for forming conclusions regarding combustion velocity in a closed space or in a gun. This experimental work is supplemented by a theoretical investigation which leads up to the determination of the internal ballistics for flake, rod, and tube powders.

From work carried out at Woolwich[184] on internal and external ballistics it was found possible to reduce the chamber capacities and charge weights in the case of several guns without affecting the ballistics; this resulted in a prolongation of the life of the guns and an economy in the financial cost per round.

For the determination of velocities an apparatus called a "ballograph" has been described.[185] It consists of two special telephones, or, if at some distance from the gun, microphones, placed 50–100in. apart, connected to the outer coil of a small transformer, the inner coil of which is connected to the needle of a galvanometer. The deviations of the needle are recorded on a travelling light-sensitive scroll of paper, on which are also recorded time intervals of 1-50—1-200 sec. produced by a helium tube actuated by a tuning fork interrupter. The head wave caused by the projectile is received by the telephones and recorded on the sensitive paper, the interval between being calculated from the helium tube records. The sound wave from the gun follows the head wave and is also recorded. Results obtained agree with those of the Boulangé apparatus and the ballograph is more generally applicable.

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[182] W. J. Huff, *J. Ind. Eng. Chem.*, 1920, **12**, 862; *J.*, 1920, 706A.

[183] Mache, *Mitt. Artillerie und Geniewesens*, 1916, 1059, 1635.

[184] Sir R. Robertson, *Nature*, 1920, 734.

[185] *Z. für tech. Physik*, 1920, 197.

An explosion pressure instrument has been devised[186] so adapted as to record the maximum pressure in a gun or to give a continuous record of the pressure. It consists of a piston bearing against the centre of a stiff spring (girder or plate) held by two knife edges on the end of a strong screw fixed to a massive frame rigidly attached to the gun. The deflection of the spring under pressure of the piston is recorded by means of the deflection of a beam of light reflected from a concave mirror fixed on the end of the spring. The beam is focussed on a rotating drum carrying a sensitive film. For maximum pressure, the drum is rotated about 1-100th of a turn during individual exposures. By rotating the drum at a peripheral speed of 30–50 m. per sec., while a continuous exposure is made, a pressure-time curve is got and from it a pressure distance curve may be deduced.

ANALYSIS OF POWDERS.

Dimethylaminoazobenzene[187] has been employed as a means of following up the decomposition of powders, particularly of the nitrocellulose type. The explosive in very fine shavings is treated with a very dilute solution of the dye. Neutral or slightly alkaline powders are coloured yellow, but if acid they become red after a time, the intensity depending on the degree of acidity. A number of excellent coloured illustrations are given, and the existence and development of nuclei of decomposition is shown. The method should be of value, particularly in the case of nitrocellulose powders, where the development of centres of decomposition is not so easily observed as in the case of nitroglycerin powders.

Smokeless powders, in the manufacture of which aromatic nitro compounds, diphenylamine, etc., are used, may be examined for the presence of nitroso compounds[188] by means of a 1% acetic acid solution of α-naphthylamine, which gives a characteristic intense violet coloration not only with nitrous acid but with nitrosoamines and nitroso derivatives. Aromatic nitro compounds contained in explosives are determined with exactness by decomposing with dilute sulphuric acid (20%) the residue from the ethereal extract from the powder, and weighing the nitro compounds thus isolated. It is very important to keep the mass continually in agitation during decomposition.

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[186] Webster, *Proc. National Acad. of Sciences*, 1919, 259.

[187] A. Angeli and G. F. Errani, *Gaz. Chim. Ital.*, 1920, **50**, I., 139 ; *J.*, **1920**, 420A.

[188] C. Butri, *Giorn. Chim. Ind. Appl.*, 1920, **2**, 557.

For the determination of mineral residue in smokeless powders, the explosive is treated repeatedly with small quantities of pyridine, evaporating each time. It is then treated with water, evaporating each time to remove volatile substances. The residue can then be ignited. If graphite is to be determined, the powder is treated with pyridine, heating from time to time on a water bath. After about 48 hours the gelatinous liquid formed at first becomes mobile, alcohol is added, and the liquid filtered through a Gooch crucible. The residue is washed with alcohol ether, warm benzene, then with dilute hydrochloric acid, and finally with water and then dried.[189]

INITIATING EXPLOSIVES.

The valuable series of volumes on explosives, published by R. Escales during recent years, has received an important addition in the 7th Volume, entitled, "Initialexplosivstoffe," by R. Escales and A. Stettbacher,[190] which has just made its way to this country. It is an excellent compendium of the subject, and brings together much of the material which has hitherto been scattered throughout the literature.

From the point of view of detonator construction, a highly interesting innovation is the open-ended tube of the Bofors Company.[191] In this form of tube, the primer is first loaded on to the top of the inner perforated cap, followed by the main charge of T.N.T. The combined charge is then well pressed. The advantages claimed are greater simplicity in loading; greater initiating power, partly as the result of better distribution of the pressure over the various portions of the charge, and partly through dispensing with potassium chlorate; greater safety, also through the absence of chlorate; greater immunity from moisture, and absence of loose fulminate, whereby sawdust "rumbling" becomes unnecessary. It is claimed that by the use of these open-ended tubes a saving of 50% of the copper used in construction is effected. Steel detonators have been used, but these deteriorate through rusting after four weeks exposure to moist air. The method of loading is patented in this country by K. G. Wennerström.[192]

Mercury fulminate still continues to be the priming material, chiefly used in detonators in this country, as well as in France and America, though in Germany there are indications that it is being displaced by lead azide. The German journals, however, still contain plentiful references to fulminate, and in this connexion mention should be made of a series of articles by A. Langhans.[193]

[189] *Ibid.*, 244; *J.*, 1920, 835A.

[190] Veit & Co., Leipsic, 1917.

[191] C. Herlin, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 137.

[192] E.P. 144,950.

[193] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 7, 9, 89; *J.*, 1920, 429A.

In the first two of these he discusses the difference between grey and white fulminate. He arrives at the conclusion that the grey substance contains an organic by-product in varying proportion. This is formed when alcohol is used, though not when paraldehyde is employed. He infers that when nascent this substance is destroyed by chlorine, but that once it is present in the crystal it resists attack by such agents as nitric acid, potassium permanganate, or hydrogen peroxide. It is possible, also, that the substance may owe its immunity to its being enclosed in the fulminate crystal. In the third of the above-mentioned papers, Langhans discusses the possibility of oxalates being present. He shows that the strength of fulminate falls away rapidly with admixture of mercuric oxalate, and suggests that the insolubility of oxalates in sodium thiosulphate solution may serve for their detection.

Langhans[194] also makes mention of an explosion which occurred at Siegburg during the dismantling of the delivery pipes of a fulminate plant. The author makes the comment that the explosive is formed in these portions of the pipes most remote from the retorts, and suggests that any fulminate which may have formed in the pipes in the vicinity of the retort would be destroyed by the issuing nitric acid and nitric oxide.

Interesting information is supplied by F. H. and P. V. Dupré.[195] The sensitiveness of mercury fulminate, even of the same sample, to direct percussion was observed to vary considerably, and it was found that the sensitiveness depended almost, if not entirely, on the size of the crystal.

A curious observation was made that fulminate-chlorate mixtures containing up to 5% of moisture were actually more sensitive to direct percussion than the dry mixture, while to combined percussion and friction they are rather less sensitive. It was also observed that a mixture containing chlorate which had passed through a 120 mesh sieve was much less sensitive to percussion but much more sensitive to friction than the fulminate from which it had been made.

Some observations are made in the same article on the dead pressing of fulminate. It would appear that fulminate in a detonator of 0·25 inch diameter can withstand a dead load of from 600 to 1500 lb. without marked deterioration, but that at 2000 lb. only one third gave good results and at 3000 lb. only one-fifth.

Two articles from the Lievin Station are published.[196] Owing to the occurrence of frequent misfires during shaft sinking in 1911, a number of electric detonators were examined. French detonators contained fulminate of mercury as priming charge with trinitrotoluene, or more generally picric acid, as main charge. The fuse head composition (*Poudre electrique*) was either mercury fulminate, copper acetylide, or a mixture of mercury thiocyanate and potassium chlorate. Curves are given for variation of firing current for detonators in series, and of resistance of single detonators with temperature, resistance with current, and for variation of temperature and current. The second portion of the papers deals with various types of exploders.

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[194] *Ibid.*, 1920, **15**, 158.

[195] *Forty-fourth Annual Report of H.M. Inspectors of Explosives for* **1919**

[196] Taffanel, D'Autriche, Turr, and Perrin, *Annales des Mines de France*, **1919, 6, 127.**

During the earlier stages of the war mercury fulminate was the initiating primer used by all the belligerents, but the advance of the Italians on Gorizia brought the Austrian quicksilver mines within range of their guns, and the Central Powers were forced to fall back on lead azide as a substitute.

P. Galewsky[197] states that the manufacture of sodium azide was taken up, albeit in an expensive and cumbersome form of apparatus. According to the author, lead azide loads badly and produces press explosions. It has the further disadvantage of being decomposed by moist air containing carbon dioxide. These difficulties, according to the author, were readily overcome by using a small top charge of lead thiocyanate.

In spite of occasional statements heard to the contrary, it is still doubtful whether lead azide can be safely loaded into detonators. A proposal to render lead azide safe by precipitating it in an amorphous form is the subject of a joint claim by W. Rintoul, J. Weir, A. G. Lowndes, and Nobel's Explosives Co.[198] The method adopted is the precipitation of the azide from the double decomposition mixture in presence of 0·5% of gelatin in the solution.

W. G. Hudson, on behalf of the du Pont Co.,[199] describes a 99–80% mixture of lead azide with 1–20% of a blasting gelatin comprising 93–70% of nitroglycerin and 7–30% of nitrocellulose. It is claimed that this is sensitive to ignition and insensitive to shock.

Lead azide appears in a patent by O. Matter[200] along with nitropentaerythrite as main charge.

A new priming material, which is already the subject of a crop of patents, is lead styphnate (lead trinitroresorcinate). A new method of preparation from styphnic acid and lead acetate is proposed by the Soc. Francaise des Munitions de Chasse de Tir et de Guerre.[201] Dr. E. von Herz claims the use of the method in fuses and explosive caps, as both primer and propellant in Flobert caps, and as an intermediate layer between T.N.T. and fulminate in detonators.[202] Proposals for its use in cap composition along with antimony sulphide, lead thiocyanate and potassium or barium styphnate and also with nitrocellulose, potassium chlorate, and powdered glass, have been made by W. H. Buell.[203]

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[197] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 190.

[198] E.P. 142,898 ; *J.*, 1920, 529A.

[199] U.S.P. 1,329,525 ; *J.*, 1920, 249A.

[200] U.S.P. 1,254,147 ; *J.*, 1918, 264A.

[201] F.P. 500,133.

A newly devised cap composition is patented by A. S. Cushman.[204] It consists of 20% antimony sulphide, 50% potassium chlorate, 25% lead thiocyanate. Instead of the 5% of T.N.T. generally used with the above ingredients, he uses 3–4% of tetryl and 2–1% of lead oxide, the latter acting as stabiliser and heat moderant.

A novel suggestion is the use of nitrated ivory nut as a main charge, which is claimed by C. M. Stine for the du Pont de Nemours Co.[205]

W. C. Cope[206] proposes the use of an 80:20 mixture of T.N.T. and tetryl in detonating fuse. It is claimed that the mixture is safe to work and easy to manipulate, that it has a higher velocity than simple T.N.T. cordeau, and that it also stands storage better.

For determining the efficiency of a cap,[207] it is proposed to use as criterion the size of the flash, measured by observing the decrease in electrical resistance in selenium. An arrangement for carrying out such an observation is suggested.

The routine tests for detonators are generally limited to the lead plate, lead block, and Esop tests. A new instrument, the bar testing machine, has recently been designed, which is capable of being adapted to testing the ordinary type of detonator. The original suggestion appears in a paper[208] by Hopkinson, where the author deals with the revolution of an impulse into its time and pressure components. The application of this test to the examination of military explosives has already been referred to.

An apparatus for determining explosion points has been devised by A. Langhans.[209] It consists of a lead block hollowed out on the under side and contained in an iron or copper box to prevent the lead from melting in contact with the flame. The block has a hole in the middle for the thermometer and four others for insertion of the test tubes containing the material to be tested.

For the determination of mercury fulminate in cap mixtures[210] it is proposed to dissolve it away with a 5% solution of potassium cyanide, depositing the mercury from the filtrate electrolytically.

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[202] E.P. 142,823.

[203] U.S.P. 1,308,393, 1,312,156; *J.*, 1919, 659A, 742A.

[204] U.S.P. 1,325,928; *J.*, 1920, 529A.

[205] U.S.P. 1,313,650; E.P. 142,303; *J.*, 1919, 742A.

[206] U.S.P. 1,341,705; *J.*, 1920, 529A.

[207] *Arms and Explosives*, 1920, 89.

[208] *Trans. Roy. Soc.*, 1914, **213**, 437.

[209] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 161; *J.*, 1920, 641A.

[210] M. Marqueyrol, *Bull. Soc. Chim.*, 1920, **27**, 488; *J.*, 1920, 528A.

H. T. Peck[211] proposes the use of a primer composition for small arms ammunition, consisting of an oxidising agent such as potassium perchlorate, and a fuel such as antimony sulphide, mercury fulminate, and di-plumbic di-trinitroresorcinate mixed in specified proportions.

Acknowledgment is made of the valuable assistance rendered by various members of the Technical Staff of Messrs. Nobel's Explosives Co. in the preparation of this section of the report.

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[211] U.S.P. 1,350,465.

ANALYTICAL CHEMISTRY.

By C. Ainsworth Mitchell, M.A., F.I.C.,

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The plan adopted in this section of the Annual Reports is the same as that followed last year, prominence being given to subjects of technical importance, which, for the most part, do not come within the scope of the Chemical Society's Report on Analytical Chemistry. The methods mentioned here have also been selected on the same principles as in the last Report, and, as before, are mainly arranged in the same order as the section headings in the *Journal.*

Apparatus and Physical Methods.

An apparatus for measuring the rate of flow of gases has been devised, which consists essentially of a capillary connected with the two limbs of a U-shaped manometer. On passing the gas through the capillary the alteration in the level of the liquid in the manometer affords a measure of the pressure of the gas. The apparatus is calibrated by determining the displacement of the liquid produced in a given time by a measured quantity of the gas at a definite pressure.[1]

A convenient form of combustion pipette for gas analysis is provided with two side tubes closed by caps which can be easily removed, and through which are sealed platinum leads attached to the ends of a platinum spiral which is fixed between the two tubes. The same principle is also applicable to capillary pipettes.[2]

A portable absorption apparatus for the analysis of gases, especially carbon dioxide in flue gases, has recently been patented.[3] The gas is pumped through the particular absorbent into a space communicating with a gauge, and the amount of constituent absorbed is estimated by measuring the degree of displacement of the piston of the pump necessary to restore the original pressure. In another apparatus based upon a similar principle, the outlet from the absorption vessel is in communication with a manometer, and the decrease in the pressure recorded affords a measure of the carbon dioxide or other absorbed constituent.[4]

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[1] J. Erlich, *Ann. Chim. Analyt.*, 1920, **2**, 280; *J.*, 1920, **766a**.

[2] E. R. Weaver and P. G. Ledig, *J. Ind. Eng. Chem.*, 1920, **12**, 368; *J.*, 1920, 531a.

[3] P. R. Boulton, E.P. 136,592; *J.*, 1920, 210a.

The use of a catalyst is claimed in several forms of apparatus for the analysis of gases. In one of these the gas is mixed with a substance capable of combining with any abnormal constituent, and the mixture is brought into contact with catalytic material, any chemical combination thus effected being indicated by a rise in the temperature.[5] In another method a current of the gas is burned in contact with a catalyst, and the amount of inflammable gas is measured by the increase of temperature of the catalyst.[6] In a somewhat analogous process the gaseous mixture is conducted over a catalyst in the vicinity either of a thermo-junction, or of one of a pair of electrically heated wires, the change in the resistance of which is measured.[7]

Measurement of the electrical resistance is also the principle adopted in another automatic method of analysis, a constant electric current being passed through a tube down which a wire is stretched. The resistance will vary with the thermal conductivity of the gas in the tubes, and consequently with its composition. At the same time the current is passed through a similar tube containing a gas for comparison.[8]

J. I. Graham's portable apparatus for determining carbon monoxide in gases[9] is not applicable to air containing motor exhaust gas, owing to the presence of the petroleum hydrocarbons. This is obviated in a new form of apparatus by condensing the hydrocarbons in U-tubes immersed in liquid air. The hydrogen, methane, and carbon monoxide are then conducted into the iodine pentoxide tube, which is heated to 100°–175° C. in an oil bath, and the liberated iodine determined as in Graham's method. Hydrogen is not oxidised at such low concentrations, and the results for carbon monoxide are accurate within 0·3–0·5 part per 10,000.[10]

It has been shown that the results given by the capillary tube method of determining the solidification point are less accurate than those obtained by immersing the thermometer in the material. Some indication of the amount of impurities in a substance is given by the form of the melting point curve, even when the melting point of the pure substance is not known.[11]

[4] F. Cossor, E.P. 138,106 ; *J.*, 1920, 283A.

[5] A. M. Kennedy, U.S.P. 1,333,850 ; *J.*, 1920, 352A.

[6] R. Naumann, G.P. 313,858 ; *J.*, 1920, 47A.

[7] A. B. Lamb and A. T. Larson, U.S.P. 1,321,063-4 ; *J.*, 1920, 47A.

[8] E. R. Weaver and others, *J. Ind. Eng. Chem.*, 1920, **12**, 359 ; *J.*, 1920, 470A.

[9] *J.*, 1919, 10T.

[10] M. C. Teague, *J. Ind. Eng. Chem.*, 1920, **12**, 964 ; *J.*, 1920, 000A.

[11] W. P. White, *J. Phys. Chem.*, 1920, **24**, 393 ; *J.*, 1920, 611A.

An apparatus for determining the electrical conductivity of metals at high temperatures has been devised on the principle of measuring the decrease in voltage along a definite length of the material through which a constant current is passed.[12]

Further applications of the use of the refractometer in analytical work have been published. For example, a formula is given for calculating the proportion of salts in aqueous solution from the refractive index. If on mixing two salts in solution precipitation occurs, the refractive index of the precipitated salt corresponds to the difference between the refractive indices of the remaining solution and those of the component solutions, and the ion concentration may be calculated from these data by means of a formula.[13] The refractive index also affords a means of calculating the proportion of paraffin wax in an oil, if the respective coefficients are known, and a formula is given for the use of the test as a control method in manufacturing processes.[14]

Reference may also be made to a new form of still head in which the passage follows a spiral course between a central core and an annular wall, only sufficient space being left for the vapour and condensed liquid to pass each other freely at the temperature of distillation.[15] The work which has been done during the past year in connexion with viscosimetry is described in the Annual Reports of the Chemical Society.

FUEL AND GAS.

The reference in last year's Report[16] to the discrepancies in the amounts of ash obtained by different chemists in the analysis of coke, did not make the point clear that the iron, which Hughes[17] found to be a main cause of the variations, is derived from the iron mortar during the pounding of the larger pieces of coke. The term "sampling" applied to this process was misleading.

The specific gravity of coal and its products may be rapidly determined by a modification of a method which has long been used for waxes. A pellet of the material is placed in sodium thiosulphate solution of sp. gr. 1·350, and the liquid diluted with water until the pellet neither rises nor sinks. The specific gravity is then found by noting the volume of water added, and referring to a table.[18]

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[12] J. L. Haughton, Faraday Soc., June 20, 1920; *J.*, 1920, 724A.

[13] M. E. Crinis, *Z. physiol. Chem.*, 1920, **110**, 254; *J.*, 1920, 766A.

[14] M. Freund and G. Palik, *Petroleum*, 1920, **15**, 757; *J.*, 1920, 650A.

[15] S. F. Dufton, E.P. 134,629; *J.*, 1920, 47A.

[16] *Ann. Repts.*, 1919, **4**, 578.

[17] *Gas World*, Feb. 1, 1919.

[18] *Gas J.*, 1920, **151**, 566; *J.*, 1920, 713A.

The methods of sampling and analysing coal have been critically examined.[19] In addition to the usual determinations, the agglutinating power [20] and increase in the volatile matter due to inert matter should also be determined.

Coke is capable of absorbing a considerable amount of moisture on exposure to the air, and it is therefore necessary to take this fact into consideration and to calculate the results of an analysis upon the dry material.[21]

An accurate method of determining sulphur in its different forms in coal has been worked out,[22] whilst for rapid estimations a modification of the method may be used, in which sulphates are extracted with boiling hydrochloric acid, and the pyrites by shaking the coal with dilute nitric acid, the organic sulphur then being obtained by difference.[23]

In view of the fact that Kjeldahl's method gives inaccurate results with fuels, a modification of Dumas' method of determining nitrogen has been devised. The material is mixed with copper oxide and heated in a silica combustion tube in contact with a copper spiral. Prior to the combustion a current of purified carbon dioxide is passed through the tube, and the process is completed by means of oxygen evolved from potassium chlorate contained in another part of the platinum boat. The gases are then collected in a nitrometer in the usual way.[24]

An apparatus for determining the volatile constituents of coal has been patented. A weighed quantity of the sample is heated in a crucible and the gases are conducted into kerosene contained in a closed flask beneath a reflux condenser. The water accumulates at the bottom, and tar is dissolved by the kerosene, whilst the gases pass on to a measuring appliance. The amount of tar is estimated from the increase in weight of the kerosene.[25]

A method of filtration through asbestos contained in a Gooch crucible is used for the estimation of tar in gas, the increase of weight being determined. Dried purified gas is passed through the apparatus before and after the passage of the gas under examination to remove moisture.[26]

Methods of estimating acetylene based on its reaction with silver nitrate and titration of the liberated acid are untrustworthy, but good results are obtained by shaking the gas or solution with freshly prepared Ilosvay's reagent,[27] separating the copper acetylide, washing it with a solution of ferric sulphate in dilute sulphuric acid, and titrating the resulting ferrous sulphate with potassium permanganate[28]—

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[19] F. S. Sinnatt, *Bull.* 4, *Lancs. and Cheshire Coal Research Assoc.*; *J.*, 1920, 538A.

[20] *J.*, 1920, 83T.

[21] W. H. Selvig and B. B. Kaplan, *J. Ind. Eng. Chem.*, 1920, **12**, 783; *J.*, 1920, 621A.

[22] A. R. Powell and S. W. Parr, *Gas J.*, 1920, **149**, 70; *J.*, 1920, 146A.

[23] A. R. Powell, *J. Ind. Eng. Chem.*, 1920, **12**, 887; *J.*, 1920, 713A.

[24] A. Parker, *Gas J.*, 1920, **150**, 624; *J.*, 1920, 155A.

[25] A. Naito, E.P. 147,254; *J.*, 1920, 642A.

[26] C. H. Stone and N. F. Prince, *Gas J.*, 1920, **151**, 238; *J.*, 1920, 591A.

$$C_2Cu_2+Fe_2(SO_4)_3+H_2SO_4=2FeSO_4+2CuSO_4+C_2H_2.$$

Reference may also be directed to a method of determining thiocyanate in ammoniacal and waste liquors from ammonia stills in the by-product coking industry.[29] Gas mask charcoal which has been highly activated forms an efficient absorbent for gasoline in natural gas, the speed at which the gas is passed through the filter tubes making but little difference in the results.[30]

MINERAL OILS ETC.

Distillation with an immiscible solvent gives the most trustworthy results in the determination of water in emulsions of petroleum etc. A mixture of commercial xylene with 20% of commercial benzene is a suitable immiscible solvent for the purpose, the volume of water in the distillate being read directly. The method also gives good results with coal-tar emulsions.[31]

The sulphur in petroleum oils may be rapidly determined by burning the oil in a calorimetric bomb, followed by titration with standard alkali. The sulphate is precipitated from a portion of the acidified solution with benzidine hydrochloride, the benzidine sulphate separated and dissolved in dilute sodium hydroxide solution, and the benzidine determined by titration with potassium permanganate.[32] Another method, suitable for vulcanised petroleum oils, consists in oxidising the oil with nitric acid and bromine, igniting the product with anhydrous sodium carbonate, and precipitating the sulphate with barium chloride from the acidified solution of the mass. The results are as accurate as those obtained with the bomb calorimeter.[33]

The various methods of estimating aromatic hydrocarbons in petrols have been studied. A method of nitration, followed by distillation and gravimetric determination of the nitro derivative gives good results when the petrol does not contain any material proportion of fractions of high b.pt. In the latter case it is preferable to heat an aliquot part of the petrol with titanous

[27] *J.*, 1899, 1158.

[28] R. Willstätter and E. Maschmann, *Ber.*, 1920, **53**, 939 ; *J.*, 1920, 509A.

[29] J. A. Shaw, *J. Ind. Eng. Chem.*, 1920, **12**, 676 ; *J.*, 1920, 564A.

[30] R. P. Anderson and C. E. Hinkley, *J. Ind. Eng. Chem.*, 1920, **12**, 735 ; *J.*, 1920, 621A.

[31] E. W. Dean and D. D. Stark, *ibid.*, 486 ; *J.*, 1920, 438A.

[32] A. W. Christie and C. S. Bisson, *ibid.*, 171 ; *J.*, 1920, 324A.

[33] C. E. Waters, *ibid.*, 482 ; *J.*, 1920, 438A.

chloride, and to titrate the excess of the reagent with a solution of a ferric salt.[34] In another modification of the nitration method the petrol is nitrated below 10° C. with nitric and sulphuric acids, and the flask filled to the mark with 95% sulphuric acid. The unattacked mineral oil separates, and its volume may be read.[35] It is essential, however, that a correction for the temperature should be made.[36]

The most suitable methods for determining the iodine value of mineral oils are those of Hübl-Waller and Wijs, but the influence of excess of iodine and duration of absorption must be ascertained for each individual product.[37]

For the detection of paraffin wax in ceresin the best method is to effect a concentration of the former by Holde's method of fractional precipitation from chloroform[38] and then to detect it by the reduction in the refractive index of the fraction.[39]

TAR AND TAR PRODUCTS.

The estimation of the nitro group in aromatic compounds by reduction with titanous chloride, as in the methods of Knecht and Hibbert, gives accurate results with many compounds. In other cases, however, notably nitrocresyl methyl ester, the results are much too high, owing to the simultaneous formation of chlorinated compounds. This error may be obviated by using titanous sulphate for the reduction, which also enables larger amounts to be used for the analysis.[40] If titanous chloride is used for the reduction of compounds to which the above-mentioned objection does not apply, it is necessary to know what excess must be added to effect complete reduction.[41]

The conductimetric method of titration with alkali solution is applicable to dilute solutions of phenols and cresols, and also for the determination of the hydroxyl group in vanillin, methyl salicylate, pyrogallol, etc.[42] A colorimetric method of determining phenol in the presence of other phenols has been based upon the fact that Millon's reagent gives a red coloration only with phenol. The only substances which interfere with the estimation are salicylic acid and β-naphthol.[43]

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[34] D. Florentin and H. Vanderberghe, *Bull. Soc. Chim.*, 1920, **27**, 204 ; *J.*, 1920, 325A.

[35] W. Hess, *Z. angew. Chem.*, 1920, **33**, 147 ; *J.*, 1920, 509A

[36] W. Hess, *ibid.*, 176 ; *J.*, 1920, 565A.

[37] W. R. Roederer, *ibid.*, 235 ; *J.*, 1920, 741A.

[38] *J.*, 1914, 242.

[39] H. Smelkus, *Chem.-Zeit.*, 1920, **44**, 273, 286 ; *J.*, 1920, 358A.

[40] T. Callan, J. A. R. Henderson, and N. Strafford, *J.*, 1920, 86T.

[41] C. F. van Duin, *Chem. Weekblad*, 1919, **16**, 1111 ; *J.*, 1920, 139A.

[42] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **112**, 187 ; *J.*, 1920, 717A.

[43] R. M. Chapin, *J. Ind. Eng. Chem.*, 1920, **12**, 771 ; *J.*, 1920, 652A

A critical examination of the methods of analysing cresylic acid has shown that Raschig's method[44] is capable of effecting the separation of as little as 1% of *p*-cresol, whilst a modification of Raschig's nitration process gives results of sufficient accuracy for technical purposes. Accurate results may also be obtained by a bromination process, in which the substance is treated in a dry solvent with dry bromine. Under these conditions *m*-cresol yields a tribromo derivative, whilst phenol, *o*-cresol, and *p*-cresol yield only dibromo derivatives. The proportion of *m*-cresol in a mixture may be calculated from the weight of bromine derivative obtained.[45]

Phenol and some of its homologues may also be estimated by a diazometric method, in which the phenol is titrated with a diazonium salt, standardised against β-naphthol solution. The method gives accurate results with phenol, cresols, and xylenols, but not with thymol.[46] A similar principle has been adapted to the determination of tar acids in the drainage from tarred roads. The method is based upon the formation of azo dyes when sulphanilic acid is diazotised and poured into water which contains the tar acids and has been made alkaline. The depth of the coloration is matched with that given by a mixture of 35% *o*-cresol, 40% *m*-cresol, and 25% *p*-cresol.[47]

To obviate the sulphonation of large quantities of toluene for the estimation of paraffins, a method has been devised in which the toluene is nitrated, the product fractionally distilled, and the distillate extracted with sulphuric acid, sulphonated, and again extracted with sulphuric acid so as to leave a residue of paraffins. This method gives fairly good results for true paraffin hydrocarbons, but does not account for all the cyclo-paraffins, which are attacked and removed to a considerable extent during the nitration and subsequent extraction.[48]

Methods based upon the reactions of aromatic amines are not applicable to the estimation of aniline in commercial anilines, owing to the common presence of toluidines as impurities. Fractional distillation also does not effect any sharp separation, but good results may be rapidly obtained by Beckmann's freezing point method. Pure dry aniline freezes at -6·0° C., and a mixture of aniline and 5% of nitrobenzene at -8·43° C.[49]

COLOURING MATTERS AND DYES.

A method of separating Yellow A.B. (benzene azo-β-naphthylamine) and Yellow OB (*o*-toluene azo-β-naphthylamine) from the other oil-soluble dyes, Butter Yellow and Soudan I, has been based upon a treatment of the mixture with petroleum spirit and sulphuric acid of different concentrations. The dyes are then identified and estimated in the fractions by means of the spectrophotometer.[50]

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[44] G.P. 114,975, 1900.

[45] J. J. Fox and M. F. Barker, *J.*, 1920, 169T.

[46] R. M. Chapin, *J. Ind. Eng. Chem.*, 1920, **12**, 568 ; *J.*, 1920, 567A.

[47] J. J. Fox and A. J. H. Gauge, *J.*, 1920, 260T.

[48] E. Lewis, *J.*, 1920, 50T.

[49] W. J. Sanderson and W. J. Jones, *J.*, 1920, 8T.

Titanous chloride may be used for the volumetric determination of diazo compounds. For example, benzenediazonium chloride may either be titrated directly, or an excess of the reagent added, and the excess titrated with a standard solution of Acid Green in the presence of sodium tartrate.[51]

ACIDS, ALKALIS, SALTS.

Graphites and Graphitic Acids.

The determination of carbon in graphites by conversion into graphitic acid by Studemann's method gives results about 1·5–2·5% higher than those obtained by Brodie's method, whilst both give a lower percentage of carbon than is obtained by direct combustion.[52] The moisture in graphitic acid cannot be determined by the usual methods, but good results are given by the method used for coal,[53] in which the substance is heated *in vacuo,* and the moisture condensed at –78° C., while gases are removed by means of a pump.[54]

Arsenic.

The results obtained by Schaeppi's method of estimating arsenic in sulphur are untrustworthy, owing to the sulphur not being quite insoluble in the dilute ammonia used for the extraction of the arsenic. A more reliable method of detection is to oxidise the sulphur by means of nitric acid and bromine, and to test the residue by Gutzeit's method.[55] Arsenic in the form of arsenious acid in sulphuric acid may be rapidly estimated by nearly neutralising the diluted acid with sodium carbonate, adding powdered sodium bicarbonate and titrating the liquid with standard iodine solution. For the estimation of arsenic acid the sulphuric acid is heated for an hour at 105°–110° C., boiled with a slight excess of sodium carbonate, and filtered. The filtrate is treated with powdered sodium bicarbonate, and then with strong hydrochloric acid and potassium iodide, and the liberated iodine titrated. The amount of calcium salts present is usually insufficient to affect the results, but if they are present to a considerable extent the proportion of potassium iodide must be increased.[56] An accurate iodometric method of estimating arsenic acid is described, in which the solution of the arsenate is heated with hydrochloric acid, and then with potassium iodide, the liberated iodine destroyed by the addition of thiosulphate, excess of sodium bicarbonate added, and the arsenious acid titrated with iodine solution. Direct titration of the iodine is inaccurate, owing to the fact that a small amount of iodine is liberated by oxygen in the solution.[57]

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[50] W. E. Mathewson, *J. Ind. Eng. Chem.*, 1920, **12**, 883; *J.*, 1920, 717A.

[51] E. Knecht and L. Thomson, *J. Soc. Dyers & Col.*, 1920, **36**, 215; *J.* 1920, 594A.

[52] W. A. Selvig and W. C. Ratcliff, *Trans. Amer. Electrochem. Soc.*, 1920, 629; *J.*, 1920, 486A.

[53] *J.*, 1917, 378.

[54] G. A. Hulett and O. A. Nelson, *Trans. Amer. Electrochem. Soc.*, 1920, 425; *J.*, 1920, 487A.

[55] H. S. and M. D. Davis, *J. Ind. Eng. Chem.*, 1920, **12**, 479; *J.*, 1920, 516A.

Acetates.

The most satisfactory method of determining the acetic acid in acetates is by distillation with phosphoric acid, and the distillation is facilitated by the use of xylene as a carrier. The distillate is titrated, and a deduction made for the hydrochloric acid produced from any chlorides in the sample.[58]

Spent Oxide.

Standard methods for sampling and testing spent oxide from gas works have been approved by the National Gas Council. The moisture is determined at 100° (3 hours) and sulphur and tar by extraction with carbon bisulphide. The residue of sulphur and tar is treated with sulphuric acid, washed and dried, and the sulphur determined by extracting the mass with carbon bisulphide.[59]

METALS AND ORES.

Iron and Steel.

The presence of silicic acid has been stated to interfere with the titration of iron with potassium permanganate in the method of Schwarz and Rolfes,[60] but experiments have been cited to show that this is not the case, and that the results are also not affected by the simultaneous presence of oxygen.[61]

The iron in iron ores may be rapidly estimated by adding to the hydrochloric acid solution an excess of standard potassium bichromate solution, and then ammonium fluoride and potassium iodide, and titrating the liberated iodine. In the presence of ammonium chloride ferric compounds do not react with the potassium iodide.[62] In using "cupferron" for the estimation of iron and its separation from manganese, corrections must be applied for the solubility of the cupferron precipitate. This solubility is reduced by adding ammonium chloride.[63]

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[56] A. A. Kohr, *J. Ind. Eng. Chem.*, 1920, **12**, 580; *J.*, 1920, 514A.

[57] P. Fleury, *J. Pharm. Chim.*, 1920, **21**, 385; *J.*, 1920, 485A.

[58] C. A. Pickett, *J. Ind. Eng. Chem.*, 1920, **12**, 570; *J.*, 1920, 585A.

[59] *Gas World*, 1920, **72**, 320; *J.*, 1920, 402A.

[60] Brandt, *J.*, 1919, 662A; 1920, 268A.

[61] R. Schwarz, *Chem.-Zeit.*, 1920, **44**, 310; *J.*, 1920, 409A.

It has been found that errors in the determination of carbon, when present in the proportion of less than 0·1% in iron, are mainly due to absorption and errors in the weighing. These errors are eliminated in a method in which the carbon dioxide is first separated by freezing with liquid air, and then allowed to expand into a known volume. The estimation is made in three stages, viz., (1) *in vacuo* in the cold; (2) at 600°C. *in vacuo*; and (3) at 1000°C. in oxygen. These distinguish between (a) carbon in the gas admitted into the tube; (b) carbon adsorbed as carbon monoxide and dioxide; and (c) that present in combination with the iron.[64] A method of estimating carbon in ferro-alloys, such as vanadium steel or chrome tungsten steel, is claimed to give results accurate within 0·002%. The alloy is electrically heated first at 450°C. *in vacuo*, and finally at 1000° in oxygen, and the carbon dioxide is absorbed in a special form of potash bulb.[65]

A rapid process of estimating sulphur in pig iron, steel, and slags and also in fuels, consists in burning the substance in oxygen at about 1280°C. and conducting the resulting gases into a solution of potassium iodide and iodate. The liberated iodine is estimated colorimetrically the comparison colour scale being prepared from potassium bichromate solution corresponding to known quantities of sulphur; or in the case of ores, slags, and fuels the iodine may be titrated.[66]

A critical study of the methods of determining phosphorus in iron, steel, ores, and slags has shown that the presence of copper, nickel, or cobalt does not affect the accuracy of the results obtained by a modification of the molybdate method, and that chromium has but little influence, but that silica and tungsten must be removed and vanadic acid reduced before the precipitation. Somewhat higher results are given by the magnesium pyrophosphate method.[67] A method of estimating phosphorus in hæmatite iron has also been described, in which the acid solution is freed from silica, and arsenic, phosphoric anhydride, and titanium separated by precipitating the iron as basic ferric phosphate. The precipitate is dissolved in hydrochloric acid, the solution oxidised with bromine, titanium separated by means of "cupferron," and the phosphorus estimated by the molybdate method.[68]

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[62] E. Little and W. L. Hult, *J. Ind. Eng. Chem.*, 1920, **12**, 200; *J.*, 1920, 409A.

[63] E. H. Archibald and R. V. Fulton, *Trans. Roy. Soc. Can.*, 1919, **13**, [iii.], 242; *J.*, 1920, 585A.

[64] T. D. Yensen, *Trans. Amer. Electrochem. Soc.*, 1920, 43; *J.*, 1920, 367A.

[65] C. J. Rottmann, *ibid.*, 59; *J.*, 1920, 367A.

[66] A. Vita, *Stahl u. Eisen*, 1920, **40**, 938; *J.*, 1920, 574A.

[67] H. Kinder, *Stahl u. Eisen*, 1920, **40**, 381, 468; *J.*, 1920, 410A.

For the volumetric estimation of iron, mercury, and vanadium in the same solution, the mercury is converted into mercuric oxide, which is dissolved in potassium cyanide solution, the excess of which is titrated with silver nitrate. The iron is reduced to the ferrous condition by means of potassium iodide in acid solution and the liberated iodine titrated. Finally, the vanadium and iron are estimated iodimetrically, and the vanadium found by difference.[69]

A rapid method of estimating tungsten in ferro-tungsten is to heat the alloy with ammonium sulphate and sulphuric acid, to dissolve the mass, and to boil the solution with nitric acid and then with hydrochloric acid to precipitate the tungstic acid.[70]

A method of analysing high-speed steel without filtration has been devised. The steel is dissolved in sulphuric acid containing silver nitrate, and the solution treated with nitric and phosphoric acids, and boiled until the tungsten disappears. Chromium, vanadium, and manganese are then successively oxidised with ammonium persulphate, and estimated by titration methods.[71] A process of extracting the bulk of the iron and molybdenum by means of ether, is used in a method of estimating zirconium and titanium in steel, these metals then being precipitated together by means of "cupferron," and the titanium subsequently determined in the mixed oxides.[72] Vanadium has some influence on the determination of chromium in high-speed tungsten steel by titration with potassium permanganate, owing to the formation of a vanadium phosphotungstate when the solution of the steel in sulphuric acid containing phosphoric acid is treated with excess of ferrous sulphate. It is therefore necessary to continue the addition of the permanganate until a red coloration changing to yellowish-brown is obtained.[73]

Mercury.

Various methods of estimating mercury gravimetrically and volumetrically have been examined, and simplified modifications of assaying the metal in ores have been devised.[74] In the standard method of the U.S. Bureau of Mines the finely powdered ore is mixed with lime and distilled into nitric acid, and the solution oxidised with potassium permanganate, the excess of which is then destroyed with hydrogen peroxide. The solution is then treated with ferric sulphate or nitrate, and titrated with potassium thiocyanate solution.[75]

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[68] N. B. Ridsdale, *Chem. News*, 1920, **120**, 219 ; *J.*, 1920, 409**A**.

[69] G. Hinard, *Ann. Chim. Analyt.*, 1920, **2**, 297 ; *J.*, 1920, 767**A**.

[70] L. Lowy, *Z. angew. Chem.*, 1919, **32**, 379 ; *J.*, 1920, 158**A**.

[71] H. O. Ward, *Chem. and Met. Eng.*, 1920, **23**, 28 ; *J.*, 1920, 574**A**.

[72] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, **1920**, **12**, 562 ; *J.*, 1920, 574**A**.

[73] P. Slawik, *Chem.-Zeit.*, 1920, **44**, 633 ; *J.*, 1920, 659**A**.

Antimony.

A new method of estimating antimony in alloys consists in dissolving the alloy in sulphuric acid containing potassium sulphate, and adding hydrochloric acid and a few drops of a dilute solution of Poirrier's Orange. The liquid is then titrated with potassium permanganate solution, the end-point being indicated by the liberation of chlorine, which bleaches the dyestuff. Lead, bismuth, tin, copper, and arsenic do not interfere with the estimation.[76]

Tin.

To obtain trustworthy results in the volumetric estimation of tin, the solution should be titrated with potassium permanganate solution in the presence of hydrochloric or sulphuric acid.[77]

Molybdenum.

The specific colour reaction which molybdenum gives with xanthic acid has been utilised in the estimation of molybdenum in steel. The coloured compound is soluble in ether, and an extract with a mixture of petroleum spirit and ether may be used for the colorimetric estimation. The presence of vanadium, tungsten, titanium, or uranium does not interfere with the reactions, but chromates, which give a dark coloration, must be reduced.[78]

Molybdenum is quantitatively precipitated by hydrogen sulphide in the presence of formic acid, provided that it is in the form of molybdate. The addition of a small proportion of an electrolyte promotes the precipitation.[79] For the volumetric estimation of molybdic acid the solution in dilute sulphuric acid may be reduced at 20°–30° C. by means of a rotating zinc cylinder in a covered beaker, and then titrated with potassium permanganate solution.[80] A method of estimating molybdenum, cobalt, and chromium in alloys has also been described, in which the molybdenum is precipitated as sulphide and weighed as oxide, the cobalt separated as hydroxide, and the chromium converted into chromate and estimated by titration with ferrous ammonium sulphate solution.[81]

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[74] R. G. Place, *Eng. and Min. J.*, 1920, **109**, 1313; *J.*, 1920, 519A.

[75] C. M. Bouton and L. H. Duschak, *U.S. Bureau of Mines, Tech. Paper* 227, 1920; *J.*, 1920, 492A.

[76] L. Bertiaux, *Ann. Chim. Analyt.*, 1920, **2**, 273; *J.*, 1920, 693A.

[77] T. G. F. Druce, *Chem. News*, 1920, **121**, 173; *J.*, 1920, 735A.

[78] S. L. Malowan, *Z. anorg. Chem.*, 1919, **108**, 73; *J.*, 1920, 27A.

[79] J. Sterba-Böhm and J. Vostrebal, *Z. anorg. Chem.*, 1920, **110**, 81; *J.*, 1920, 351A.

[80] W. Scott, *J. Ind. Eng. Chem.*, 1920, **12**, 578; *J.*, 1920, 530A.

Tellurium.

When potassium anhydrotellurate is suspended in dilute hydrochloric acid and treated with zinc, tellurium is quantitatively precipitated as a powder.[82] Advantage has been taken of this reaction for the estimation of tellurium in tetradymite. The mineral is freed from silica, the nitric acid solution evaporated to dryness, and the residue fused with potassium nitrate. Potassium sulphate and selenate are then extracted with boiling water, and bismuth oxide with dilute hydrochloric acid, and the residual potassium anhydrotellurate reduced to tellurium, which is separated and weighed.[83]

FATS, OILS, AND WAXES.

The melting point, determined under standard conditions, will afford an indication of the amounts of constituents of dual mixtures of fats, such as palm-kernel or coconut oil with each other or with arachis oil. In the case of mixtures of three components, however, a second constant, such as the refractive index, is required, and test experiments showed that in the case of the three fats mentioned the percentage composition was proportional to the refractive index, whilst the addition of 10% of arachis oil lowered the m.p. by only 0·4° C. By plotting the refractive indices as ordinates and the melting points as abscissæ, a closed graph is obtained, which may be divided into sections for estimating the constituents of dual or triple mixtures. It is necessary, however, to make an allowance for the effect of natural variation in the crude products upon the refined fats.[84]

Experiments upon the use of butyl alcohol as a medium in the determination of the saponification value have shown that in the case of substances difficult to saponify, such as beeswax, spermaceti, and wool fat, the results are higher and more accurate after 30 minutes' saponification in presence of *n*-butyl alcohol, than by the usual method. Saponification is complete after 5 minutes in the case of oils, such as codliver oil.[85]

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[81] J. R. Camp and J. W. Marden, *J. Ind. Eng. Chem.*, 1920, **12**, 998; *J.*, 1920, 753A.

[82] P. Hulot, *Bull. Soc. Chim.*, 1920, **27**, 33; *J.*, 1920, 189A.

[83] P. Hulot, *ibid.*, 100; *J.*, 1920, 238A.

[84] F. H. Trim, *J.*, 1920, 307T.

[85] A. M. Pardie, R. L. Haseltine, and E. E. Reid, *J. Ind. Eng. Chem.*, 1920, **12**, 481; *J.*, 1920, 458A.

Further comparative studies of the different methods of determining the iodine value have been published.. The results obtained with pure elaidic acid by the method of Hanus agreed more closely with the theoretical value than those given by the methods of Hübl, Waller, Winkler, or Wijs.[86] On the other hand, in similar test determinations on linolic acid Hübl's method gave the best results.[87]

A trustworthy method of distinguishing between hydrogenated marine animal oils and hydrogenated rape oil has been based upon the determination of the molecular weight of the fatty acids of lower b.p. fractionated under reduced pressure. Only the hydrogenated marine animal oil contains acids with molecular weight lower than that of palmitic acid, whilst hydrogenated rape oil yields no fraction with molecular weight exceeding 201.[88]

The use of a 10% solution of monosodium phosphate as a solvent for the extraction of uncombined sulphate from sulphonated oils gives trustworthy results in a much shorter time than extraction with brine and ether. Total sulphate is best determined by evaporating the oil with sodium carbonate, fusing the residue, boiling the solution of the fused mass with sodium peroxide, and precipitating the sulphuric acid as barium sulphate.[89]

Nastjukoff's formolite reaction has been adapted to the estimation of traces of petroleum spirit in vegetable oils. The oil is saponified, the soap solution treated with calcium chloride and distilled, and 40% formaldehyde solution and a few drops of sulphuric acid added to the distillate. In the presence of petroleum spirit a red-brown film will be formed. The test may be made quantitative by separating the formolite precipitate and weighing it after drying at 110°–115° C.[90]

MEDICINAL PRODUCTS, ORGANIC SUBSTANCES.

Iron in Pharmaceutical Syrups.

A volumetric method of estimating iron in the presence of hydrochloric acid, phosphorus oxy-acids, and organic matter has been worked out. The slightly acidified syrup is treated with a very slight excess of potassium permanganate, and then with an equal volume of concentrated hydrochloric acid and sodium carbonate to give an atmosphere of carbon dioxide. It is then treated with standard stannous chloride solution until a drop of the liquid gives a blue coloration with potassium ferrocyanide, and finally titrated with the stannous chloride solution, with potassium thiocyanate as outside indicator.[91]

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[86] W. Devrient, *Ber. deuts. pharm. Ges.*, 1920, **30**, 361; *J.*, 1920, 755A.

[87] T. Sundberg and M. Lundberg, *Z. Unters. Nahr. Genussm.*, 1920, **39**, 87; *J.*, 1920, 604A.

[88] A. Grün, *Chem. Umschau*, 1920, **26**, 101.

[89] E. J. Kern, *J. Ind. Eng. Chem.*, 1920, **12**, 785; *J.*, 1920, 692A.

[90] M. Aida, *J.*, 1920, 152T.

Phenyl Derivatives of Arsenious Acid.

For the analysis of mixtures of arsenious chloride, phenylarsine, and diphenylarsine the mixture is dissolved in benzene and the solution extracted with sodium hydroxide solution. Iodometric titration of the extract diluted with alcohol and acidified gives the phenylarsine, whilst continuation of the titration after the addition of sodium bicarbonate gives the arsenious chloride. The residual benzene solution is titrated with iodine to obtain diphenylarsine and triphenylarsine chlorides, the latter of which may be separated by extraction with chloroform after the addition of sodium bicarbonate.[92]

Tetranitromethane.

On shaking tetranitromethane with aqueous alkaline solutions of reducing agents, nitroform is produced. The reaction is quantitative with aqueous solutions of hydrazine, and measurement of the nitrogen evolved affords a means of estimating tetranitromethane. Conversely that substance may be used for estimating hydrazine in solutions of its salts.[93]

Glycol.

The bichromate and acetin methods used in the analysis of glycerin may also be employed for the accurate estimation of glycols, but in the case of the latter method the solution of the glycol must be concentrated. The results obtained by oxidation with chromic acid and sulphuric acid and estimation of the carbon dioxide are also accurate, but oxidation with potassium permanganate does not give a quantitative yield of oxalic acid.[94]

Alkaloids.

The conductimetric method of titration gives good results with alkaloids. Salts may be directly titrated with alkali without the addition of alcohol, but for acid titration a solution in 50% alcohol should be used.[95]

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[91] H. D. Richmond and E. M. Ison, *Analyst*, 1920, **45**, 258 ; *J.*, 1920, 585A.

[92] P. Fleury, *Bull. Soc. Chim.*, 1920, **27**, 699 ; *J.*, 1920, 638A.

[93] A. Baillie, A. K. Macbeth, and N. I. Maxwell, *Chem. Soc. Trans.*, 1920, **117**, 880 ; *J.*, 1920, 639A.

[94] B. Müller, *Chem.-Zeit.*, 1920, **44**, 513 ; *J.*, 1920, 642A.

[95] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **112**, 196 ; *J.*, 1920 733A.

ABBREVIATIONS USED IN FOOTNOTES.

THE following is a list of journals &c. to which reference is made in this volume, with the abbreviations used. Where the title has not been abbreviated it is given in the first column only.

Agric. Res. Inst. Pusa Indigo Pub.	Agricultural Research Institute, Pusa, Indigo Publications.
Alkali Inspector's Rep.	Reports of the Chief Inspector under the Alkali Works Act.
Allg. Brau- u. Hopfenzeit.	Allgemeine Brau- und Hopfenzeitung.
Allg. Z. Bierbr. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Machinist	American Machinist.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica Quimica.
Anal. Soc. Quim. Argentina	Anales de la Sociedad Quimica Argentina.
Analyst.	
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Brass. et Dist.	Annales de la Brasserie et de la Distillerie.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Repts.	Annual Reports of the Progress of Applied Chemistry.
Apoth.-Zeit.	Apotheker-Zeitung.
Arch. Pharm.	Archiv der Pharmazie.
Archief Suikerind. Ned. Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Archief voor de Rubbercultuur.	
Ark. Kem., Min., o. Geol.	Arkiv for Kemi, Mineralogi, och Geologi.
Arms and Explosives.	
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Automobile Eng.	Automobile Engineering.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deuts. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationeller Landwirtschafts-Betrieb.
Biochem. J.	Biochemical Journal.
Biochem. Zeits.	Biochemische Zeitschrift.
Blast Furnace and Steel Plant.	
Bd. of Trade J.	Board of Trade Journal.
Brasserie et Malterie.	

Brennstoff-Chem.	Brennstoff-Chemie.
Brewing Trade Review.	
Brit. Med. J.	British Medical Journal.
Brit. J. Phot.	British Journal of Photography
Bull. Agric. Intell.	Bulletin of Agricultural Intelligence and Plant Diseases.
Bull. Amer. Inst. Min. Eng.	Bulletin of the American Institute of Mining Engineers.
Bull. Assoc. Anc. Elèves de Louvain	Bulletin de l'Association des Anciens Élèves de Louvain.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association Chimique de Sucre et de Distillerie.
Bull. Eng. Expt. Sta., Illinois Univ.	Bulletin of the Engineering Experiment Station, University of Illinois.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Lancs. & Ches. Coal Res. Assoc.	Bulletin of the Lancashire and Cheshire Coal Research Association.
Bull. Rubber Growers' Assoc.	Bulletin of the Rubber Growers' Association.
Bull. Soc. Chim.	Bulletin de la Société Chimique de France.
Bull. Soc. Chim. Belg.	Bulletin de la Société Chimique de Belgique.
Bull. Soc. Chim. Biol.	Bulletin de la Société de Chimie Biologique.
Bull. Soc. Chim. Maurice	Bulletin de la Société Chimique de Maurice.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie.
Bull. Soc. Ind. Min.	Bulletin de la Société de l'Industrie Minière.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Camera Craft.	
Canad. Chem. J.	Canadian Chemical Journal.
Caoutchouc et Guttapercha.	
Cellulosechemie (Beiblatt to Papierfabrikant).	
Chem. Age	Chemical Age.
Chem. Ind.	Chemische Industrie.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. News	Chemical News.
Chem. Soc. Trans.	Transactions of the Chemical Society.
Chem. Trade J.	Chemical Trade Journal.
Chem. Umschau	Chemische Umschau ueber die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Chim. et Ind.	Chimie et Industrie.
Circ. Paint Manufrs. Assoc. U.S.	Circulars of the Paint Manufacturers Association of the United States.
Cmd.	Government Publications.
Collegium.	
Comptes rend.	Comptes rendus hebdomadaire des Séances de l'Academie des Sciences.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux de Laboratoire de Carlsberg.
Comm. Netherland Govt. Inst. for Advising Rubber Trade	Communications of the Netherland Government Institute for Advising the Rubber Trade and Rubber Industry.
Cotton Oil Press.	
Der Photograph.	
Deuts. Med. Woch.	Deutsche Medizinische Wochenschift.
Deuts. Zuckerind.	Deutsche Zuckerindustrie.
Die Photographie.	
Die Siefer	Drugs, Oils, and Paints.
Drugs, Oils, and Paints.	
E.P.	English Patent.
Elect. World	Electrical World.

Electrician.	
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News Rec.	Engineering News Record.
F.P.	French Patent.
Farben-Zeit.	Farben-Zeitung.
Färber-Zeit.	Färber-Zeitung.
Fermentforsch.	Fermentforschung.
Foundry.	
G.P.	German Patent.
Gas J.	Gas Journal.
Gas World.	
Gaz. Chim. Ital.	Gazzetta Chimica Italiana.
Geographical Review.	
Ges. Abhandl. Kennt. Kohle.	Gesammelte Abhandlungen zur Kenntniss der Kohle.
Giorn. Chim. Ind. Appl.	Giornali di Chimica Industriale ed Applicata.
Glückauf.	
Gummi-Zeit.	Gummi-Zeitung.
Helv. Chim. Acta	Helvetica Chimica Acta.
Il Progresso Fotog.	Il Progresso Fotografico.
India-Rubber J.	India-Rubber Journal.
India-Rubber World.	
Inst. Pet. Tech.	Institution of Petroleum Technologists.
Intern. Sugar J.	International Sugar Journal.
Iron Age.	
Iron and Coal Trades Rev.	Iron and Coal Trades Review.
Iron and Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.	Journal of the Society of Chemical Industry.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Cer. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Chem. Ind. Tokyo	Journal of Chemical Industry, Tokyo.
J. Coll. Eng., Tokyo Imp. Univ.	Journal of the College of Engineering, Tokyo Imperial University.
J. Fab. Sucre	Journal des Fabricants du Sucre.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gasbeleucht.	Journal für Gasbeleuchtung.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Ind. Hygiene	Journal of Industrial Hygiene.
J. Ind. Inst. Sci.	Journal of the Indian Institute of Science.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Elect. Eng.	Journal of the Institution of Electrical Engineers.
J. Inst. Mech. Eng.	Journal of the Institution of Mechanical Engineers.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. San. Eng.	Journal of the Institution of Sanitary Engineers.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Minis. Agric.	Journal of the Ministry of Agriculture.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.

J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan.
J. Phys. Chem.	Journal of Physical Chemistry.
J. prakt. Chem.	Journal für praktische Chemie.
J. Roy. San. Inst.	Journal of the Royal Sanitary Institute.
J. Roy. Soc. Arts	Journal of the Royal Society of Arts.
J. S. Afr. Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech.	Journal of the Society of Glass Technologists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
J. Trop. Med. Hyg.	Journal of Tropical Medicine and Hygiene.
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences.
J. West of Scotland Iron and Steel Institute.	
Koll.-Chem. Beih.	Kolloid-Chemische Beihefte.
Kolloid-Zeits.	Kolloid-Zeitschrift.
La. Bulletin	Louisiana Bulletin.
La Céramique.	
L'Age de Fer.	
La. Planter	Louisiana Planter.
Lancet.	
La Papeterie.	
Landw. Jahrb. Schweiz	Landwirtschaftlichen Jahrbuch der Schweiz.
Leather Trades' Review.	
Le Génie Civil.	
Le Papier.	
Ledertechn. Runds.	Ledertechnische Rundschau.
L'Industria.	
Med. Geneesk. Lab. Weltevreden.	Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden.
Medd. K. Vetenskakad. Nobel-Inst.	Meddelanden fran Kongl-Vetenskapsakademiens Nobel-Institut.
Metal Ind.	Metal Industry.
Metall u. Erz	Metall und Erz.
Milchw. Zentr.	Milchwirts chaftliche Zentralblatt.
Min. Mag.	Mining Magazine.
Min. and Sci. Press	Mining and Scientific Press.
M. Min. Inv. Dept.	Ministry of Munitions Inventions Department.
Mitt. K. Materialprüf.	Mitteilungen aus dem Königlichen Materialprüfungsamt zu gross-Lichterfelde West.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebeite der Lebensmitteluntersuchungen und der Hygiene.
Mitt. Inst. Kohlenvergasung	Mitteilungen des Instituts für Kohlenvergasung und Nebenprodukengewinnung.
Monatschr. Textilind.	Monatschrift für Textil-Industrie.
Monatsh. Chem.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
National Glass Budget.	
Neue Faserstoffe.	
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Oil and Gas J.	Oil and Gas Journal.
Paint Manufrs. Assoc. U.S.	Paint Manufacturers Association of the United States.
Paper.	
Paper Makers' Monthly Journal.	
Papierfab.	Papierfabrikant.
Perf. Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (German).
Petroleum Age.	
Pflüger's Arkiv.	Arkiv für die Gesammte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.

Pharm. Zentralh.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine and Journal of Science.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Phot. Rund.	Photographische Rundschau.
Phys. Soc.	Physical Society.
Physiol. Abs.	Physiological Abstracts.
Pottery Gazette.	
Proc. Amer. Acad.	Proceedings of the American Academy of Sciences.
Proc. Amer. Soc. Testing Materials	Proceedings of the American Society for Testing Materials.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. K. Akad. Wetensch.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Edition).
Proc. Oil and Colour Chem. Assoc.	Proceedings of the Oil and Colour Chemists' Association.
Proc. Phys. Soc.	Proceedings of the Physical Society.
Proc. Phys.-Math. Soc. Japan	Proceedings of the Physico-Mathematical Society of Japan.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. and Med.	Proceedings of the Society of Experimental Biology and Medicine.
Prog. Ind. Tint. Tess.	Progresso degli Industrie Tintoriale ed Tessile.
Przemysl-Chem.	Przemysl-Chemie.
Pulp and Paper Mag.	Pulp and Paper Magazine of Canada.
Rec. Trav. Chim.	Recueil des Travaux Chimiques de Pays-Bas.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Prod. Chim.	Revue de Produits Chimiques.
Rubber Age	Rubber Age and Tire News.
San. Rec.	Sanitary Record.
Schweiz. Chem. Zeit.	Schweizerische Chemiker-Zeitung.
Seifens.-Zeit.	Seifensieder-Zeitung.
Sitzungsber. Preuss. Akad. Wiss.	Sitzungsberichte der Königlichen Preussischen Akademie der Wissenschaften.
Soil Sci.	Soil Science.
Sprechsaal.	
Sprengstoffe, Waffen, und Munitionen.	
Stahl u. Eisen	Stahl und Eisen.
Staz. Sper. Agrar. Ital.	Stazione Sperimentali Agraria Italiana.
Surveyor.	
Svensk Farm. Tidskr.	Svensk Farmaceutisk Tidskrift.
Technique Moderne	
Text. Forsch.	Textil Forschung.
Times Eng. Suppl.	Times Engineering Supplement.
Tonind.-Zeit.	Tonindustrie-Zeitung.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Cer. Soc.	Transactions of the Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Gas Eng.	Transactions of the Institution of Gas Engineers.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.

Trans. N.E. Coast Inst. Eng.	Transactions of the North East Coast Institution of Engineers and Shipbuilders.
Trans. Roy. Soc. Canada.	Transactions of the Royal Society of Canada.
U.S. Bureau of Mines, Bull. and Tech. Papers	U.S. Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau of Standards.	
U.S. Comm. Rep.	U.S. Commerce Reports.
U.S. Dept. Agric. Bull.	Bulletins of the U.S. Department of Agriculture.
U.S. Naval Inst. Proc.	U.S. Naval Institute Proceedings.
U.S.P.	U.S. Patent.
Wien. landwirts. Zeit.	Wiener landwirtschaftlicher Zeitung.
Woch. Brau.	Wochenschrift für Brauerei.
Woch. Papierfabr.	Wochenblatt für Papierfabrikation.
Z. angew. Botanik.	Zeitschrift für angewandte Botanik.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische Chemie.
Z. f. Dampfkessel	Zeitschrift für Dampfkessel und Maschinenbetrieb.
Z. Elektrochem.	Zeitschrift für Elektrochemie und angewandte physikalische Chemie.
Z. ges. Brauw.	Zeitschrift für das gesammte Brauwesen
Z ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
Z. Metallkunde	Zeitschrift für Metallkunde.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Z. physik. Chem	Zeitschrift für physikalische Chemie.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Sauerst.- u. Stickstoffind.	Zeitschrift für Sauerstoff- und Stickstoffindustrie.
Z. Techn. Biol.	Zeitschrift für technische Biologie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs und Genussmittel.
Z. Ver. deuts. Ing.	Zeitschrift des Vereins deutscher Ingenieure.
Z. Ver. deuts. Zuckerind.	Zeitschrift des Vereins deutscher Zuckerindustrie.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.
Z. Zuckerind. Czechoslov.	Zeitschrift für Zuckerindustrie in Czechoslovakischen Republik.
Zement.	
Zentr. Bakt.	Zentralblatt für Bakteriologie.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

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ERRATA IN INDEX OF VOL. IV.

Page 605, col. 2, for "Parker, R. G., 15, 35," read
"Parker, A., 35.
Parker, R. G., 15."

Page 608, col. 2, for "Spielmann, A., 545, 582, 583, 584," read
"Spielmann, A., 545.
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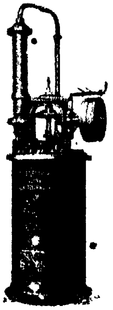

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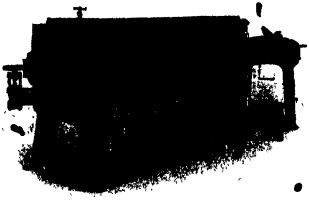

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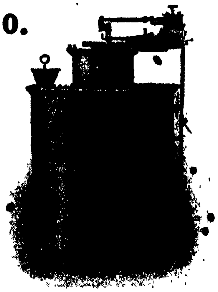

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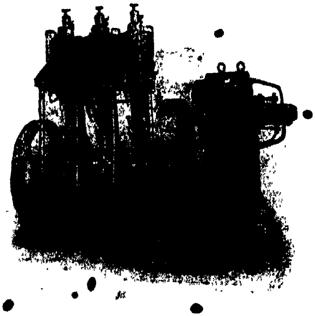

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